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# Controls on denitrification in a northeastern coastal suburban riparian zone

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CONTROLS ON DENITRIFICATION IN A NORTHEASTERN  
COASTAL SUBURBAN RIPARIAN ZONE

BY

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B.S., University of Colorado at Boulder, 2003

THESIS

Submitted to the University of New Hampshire  
in Partial Fulfillment of  
the Requirements for the Degree of

Master of Science

in

Natural Resources

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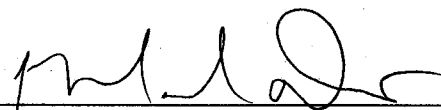
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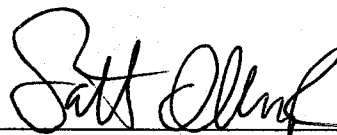
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12/5/07

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Date

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## ABSTRACT

### CONTROLS ON DENITRIFICATION IN A NORTHEASTERN COASTAL SUBURBAN RIPARIAN ZONE

By

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University of New Hampshire, December, 2007

Anthropogenic nitrogen (N) inputs in terrestrial and aquatic ecosystems can alter groundwater N cycling, which affects N fluxes in surface water and coastal environments. Increased N inputs can decrease the overall health of terrestrial and coastal ecosystems as well as pose serious human health threats. It is well documented that riparian zones can reduce N fluxes to surface water bodies as well as coastal environments. Recently, it has been determined that riparian denitrification potential is largely influenced by hydrogeologic characteristics.

Hydrogeologic characteristics and groundwater physical properties and chemical constituents were evaluated in the James Farm well field located in Lee, NH, USA from 1995 to 1996, and 2004 to 2006. The “push-pull” method estimated denitrification potential by adding different quantities of nitrate and dissolved organic carbon to riparian groundwater. The constituents measured were nitrate, ammonium, total dissolved nitrogen, dissolved organic carbon, sulfate, bromide, chloride, sodium, magnesium, potassium, calcium, and silica. Patterns of nitrogen concentration in ambient riparian groundwater suggested

that denitrification might be occurring as groundwater flowed through the center of the well field. Field experiments with the push-pull method, however, showed that substantial N loss did not occur even with large amounts of added nitrate and dissolved organic carbon. Short groundwater residence times may have been responsible for the lack of denitrification. Because human population density is significantly correlated with  $\text{NO}_3^-$  concentrations in surface- and groundwater, and global human population continues to grow exponentially, an increase in  $\text{NO}_3^-$  concentrations is likely. It is essential to further examine denitrification control mechanisms to determine if riparian zones are important in regulating nitrogen loss from coastal New Hampshire watersheds.

## INTRODUCTION

The encroachment of suburban areas into previously undisturbed forests, shrublands, and deserts represents a dominant demographic trend that is altering ecosystem processes (Katz and Bradley, 1999). Approximately half of the world's population lives within these urban areas, and this percentage is estimated to increase 60% by the year 2030 (Hobbs and Stoops, 2002). In 2000, the Northeastern United States was the most densely populated area in the country with the highest percentage of people living within suburban areas (Hobbs and Stoops, 2002). Anthropogenic activities can alter nutrient cycles (Carpenter et al., 1998; Barrios, 2000; USGS, 2001; Kaushal et al., 2005). More specifically, anthropogenic nitrogen (N) inputs in terrestrial and aquatic ecosystems can alter groundwater N cycling, which affects N fluxes in surface water and coastal environments (Vitousek and Howarth, 1991; Vitousek et al., 1997). In addition, human population density is linked to increases in surface water nitrate ( $\text{NO}_3^-$ ) concentrations as well as influencing  $\text{NO}_3^-$  export (Daley, 2002; O'Donnell, 2004). This increase in population density, and associated changes to the N cycle, makes the Northeastern U.S. an ideal study site for how suburbanization affects changes in N fluxes through the surrounding terrestrial and aquatic ecosystems.

Increased inputs of  $\text{NO}_3^-$  and ammonium ( $\text{NH}_4^+$ ) into terrestrial and aquatic ecosystems is caused by anthropogenic activities such as, combustion of fossil

fuels, automobile exhaust, pollution from industrial smokestacks, food and feed imports, septic systems, sewage treatment plants, and residential and agricultural fertilizers. Nitrogen emitted to the atmosphere can be deposited to terrestrial and aquatic habitats directly from dry deposition, precipitation, and throughfall and eventually infiltrate soils and groundwater. Septic tanks have leach fields that also increases N inputs into the soil and groundwater. In addition, there have been direct N inputs (as  $\text{NH}_4^+$ ) from fertilizer use in an effort to boost crop production to meet the needs of the growing human population (Galloway and Cowling, 2002). The increased input of N into groundwater can eventually enter into drinking water sources or surface water leading to adverse consequences for human health and ecosystem processes.

Increased N input harms aquatic life, reduces biodiversity, and contaminates fish species and drinking water creating harmful, if not deadly, conditions for humans (Weyer, 2001; Rabalais, 2002). Increased  $\text{NO}_3^-$  inputs into streams and lakes can result in algal blooms. Algal blooms can block sunlight needed by plants located beneath the algae, resulting in less oxygen production. When the algae decompose, dissolved oxygen levels decrease creating hypoxic/anoxic conditions. This decreases the overall health for the aquatic life and can result in fish kills. Furthermore, an increase in  $\text{NH}_4^+$  inputs can lead to increased nitrification rates, which results in surface- and groundwater acidification. Acidic groundwater can leach metals such as aluminum and mercury into surface- and groundwater drinking water sources. Aluminum affects fishes' gills and can reduce biodiversity within these aquatic

ecosystems (EPA, 2002; Driscoll et al., 2003). In addition, mercury accumulates in the higher trophic levels of food webs, which results in contamination of predatory fish species. Some commercial fish species contaminated with mercury now pose serious human health risks and substantial economic costs (Fitzgerald and Clarkson, 1991).

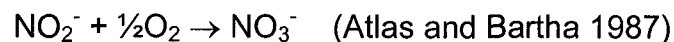
Nitrate contamination of drinking water sources can also compromise human health (Tsezou et al., 1996; Mueller et al., 2001). Due to these health risks,  $\text{NO}_3^-$  in drinking water has a maximum contaminant level (MCL) of 10 mg N  $\text{L}^{-1}$  as regulated by the Environmental Protection Agency (EPA). One health risk is methemoglobinemia (also known as blue baby syndrome) where oxygen ( $\text{O}_2$ ) delivery to blood cells is disturbed as a result of  $\text{NO}_3^-$  sharing an electron with iron molecules in hemoglobin instead of  $\text{O}_2$ . Oxygen is not attached to blood cells and is not delivered to other parts of the body (Austin, 1999; Knobeloch et al., 2000; Soares, 2000). Moreover,  $\text{NO}_3^-$  can be reduced to nitrite ( $\text{NO}_2^-$ ), which can react chemically with amino acids to form highly carcinogenic nitrosamines (Ward et al., 1996). Because an estimated 42% of the U.S. population uses groundwater as their drinking water supply, there is an overwhelming need to understand how urbanization affects groundwater N cycling (Hutson et al., 2004).

### **Nitrogen Cycling Processes**

To fully understand the impacts of urbanization on the N cycle, it is important to understand how N processes occur under natural conditions. Processes influencing N species composition include mineralization, immobilization, nitrification, and denitrification.

Mineralization is the decomposition of organic N to  $\text{NH}_4^+$  and can create a significant pool of N that is susceptible to hydrologic or gaseous loss (Likens et al, 1970, Foster et al. 1989). Organic N produced by decomposition of leaf litter, plant root exudation, and animal excrement can leach into the soil profile. Plant litter containing larger nutrient concentrations decomposes more quickly causing mineralization to begin earlier (Schlesinger, 1997). Microbes can immobilize N during decomposition, which can slow the process of N leaching into groundwater. Microbial immobilization of N occurs mostly within the fresh litter on the soil surface while mineralization occurs within the lower forest floor (Federer, 1983; Qualls et al., 1991).

Nitrification is the oxidation of  $\text{NH}_4^+$  or ammonia ( $\text{NH}_3^+$ ) to  $\text{NO}_2^-$  and then  $\text{NO}_3^-$ . A restricted number of chemoautotrophic bacteria conduct nitrification, which only occurs in aerobic conditions (Atlas and Bartha, 1987).

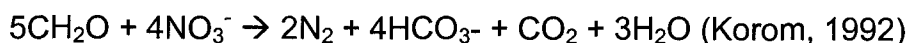


The oxidation of  $\text{NH}_4^+$  to  $\text{NO}_3^-$  is coupled to the fixation of carbon (C) by these bacteria (Schlesinger, 1997). Nitrification yields hydrogen ions ( $\text{H}^+$ ) that lower the pH within the surrounding environment. The change from positive to negative charge in the transformation of  $\text{NH}_4^+$  to  $\text{NO}_3^-$  is important because positively charged ions tend to bind to the negatively charged soil particles (Atlas and Bartha, 1987). Because  $\text{NO}_2^-$  and  $\text{NO}_3^-$  are negatively charged, these N



species mobilize and migrate freely through the soil water (Atlas and Bartha, 1987). Therefore,  $\text{NO}_3^-$  can accumulate in groundwater and leach into streams and lakes. Sources of  $\text{NO}_3^-$  in aquatic habitats include  $\text{NO}_3^-$  diffusion into sediment from the water column,  $\text{NO}_3^-$  leached into sediments via groundwater, and  $\text{NO}_3^-$  produced in sediments by nitrification of  $\text{NH}_4^+$ .

Potential  $\text{NO}_3^-$  losses are currently difficult to measure and poorly understood. Nitrate losses in soil and groundwater can occur by denitrification, microbial immobilization, and dilution (Mulholland, 1992). Factors controlling denitrification rates are temperature, dissolved oxygen (DO) concentrations, and soil chemical composition and moisture. Heterotrophic microbes, generally facultative anaerobic bacteria, conduct denitrification under reducing conditions by converting  $\text{NO}_2^-$  or  $\text{NO}_3^-$  into  $\text{N}_2\text{O}$ ,  $\text{NO}$ , or  $\text{N}_2$  gas and occurs by the following reaction (Seitzinger, 1988).



Temperature and DO concentrations affect the rate at which heterotrophic microbes denitrify. As temperatures rise, microbes' metabolisms increase, which enables nitrifying bacteria to increase  $\text{NO}_3^-$  concentrations within the groundwater and denitrifying bacteria to convert  $\text{NO}_3^-$  into  $\text{N}_2\text{O}$  or  $\text{N}_2$ , thus reducing  $\text{NO}_3^-$  concentrations. Increased microbial metabolic rates also decrease  $\text{O}_2$  concentrations that could result in anoxic zones due to the slow rate of  $\text{O}_2$  diffusion into water. Soil microbes use  $\text{O}_2$  as a terminal electron acceptor

to fulfill energy requirements during the oxidation of organic matter. However, when anoxic conditions exist, microbes can reduce  $\text{NO}_3^-$  or  $\text{NO}_2^-$  to fulfill energy requirements (Payne, 1973; Soares, 2000). The reduction of  $\text{NO}_3^-$  or  $\text{NO}_2^-$  by denitrifiers occurs in slightly oxic to anoxic conditions. This ability to reduce  $\text{NO}_3^-$  can further decrease  $\text{NO}_3^-$  concentrations, resulting in less  $\text{NO}_3^-$  for microbes to denitrify. However, increasing inputs of anthropogenic  $\text{NO}_3^-$  into soil and groundwater alleviates  $\text{NO}_3^-$  limitation for denitrifiers.

The availability of labile and humic carbon (C) in soil influences N cycling because microbes need carbon as an energy source (Meyer et al., 1987). Heterotrophic bacteria require organic C, whereas autotrophic bacteria use carbon dioxide ( $\text{CO}_2$ ) as a carbon source. Autotrophic bacteria fulfill energy requirements from sulfide (chemoautotrophs) or sunlight (cyanobacteria). The autotrophic bacteria acquire  $\text{CO}_2$  that is released during microbial respiration. Carbon can become a limiting nutrient when small concentrations of organic C are available for microbes, which results in less  $\text{CO}_2$  released from microbial respiration. However, if there is a higher C:N ratio, the metabolic need for N in the microbial community is increased; thus, there is competition for available  $\text{NH}_4^+$  between heterotrophic and autotrophic bacteria. Even though the competition for available  $\text{NH}_4^+$  is high for autotrophic bacteria because heterotrophic bacteria are typically more abundant and grow faster than autotrophic bacteria (Prosser, 1989), agricultural land or areas with high human population densities increase inorganic N abundance compared to natural ecosystems, thus possibly alleviating  $\text{NH}_4^+$  competition. Abundant sources of

inorganic N can result in energy (C) limitation of microbial growth.

Humic soil is comprised of greatly altered organic matter that is an intermediate product of decomposing plant and animal remains. Humic soils are present at greater soil depths; thus, possibly affecting chemistry in groundwater located in deeper soils. The soil-derived dissolved organic carbon (DOC) possibly comprised of humic acids make it difficult for microbial breakdown (Thurman, 1985; McDowell and Likens, 1988). A low-lignin C food source makes it difficult for denitrifiers to convert  $\text{NO}_3^-$  to  $\text{N}_2$ . However, labile C requires less energy for microbes to breakdown. Labile C in organic matter derived from root exudates and leaf litter can enter the groundwater and used as an energy source by  $\text{NO}_3^-$  reducing microbes (Pinay et al., 1993). A substantial amount of labile C in the soil can increase denitrification rates in anaerobic environments.

### **Riparian Zones**

Areas of land between stream channels and upland areas that frequently experience anoxic conditions, known as riparian zones, can be sites of substantial N removal from soil and groundwater by denitrification. Many studies have determined that denitrification rates can significantly reduce N concentrations within the upper surface in riparian soils (Vogel et al., 1981; Lowrance et al., 1984; Jacobs and Gilliam, 1985; Cooper, 1990; Groffman et al., 1992; Pinay et al, 1993; Hill, 1996; Correl, 1997; Clement et al, 2002). Several studies suggest that for denitrification to occur DO concentrations must be  $<2\text{-}3 \text{ mg L}^{-1}$  (Cey et al., 1999; Hill et al., 2000). Because denitrification occurs in anoxic conditions and  $\text{O}_2$  slowly diffuses into groundwater, denitrification is

favorable to occur within saturated soils. Favorable conditions for denitrification exist in shallow groundwater tables with hydric soils (Gold et al, 2001).

Denitrification is favored when groundwater intercepts organic-rich soils (Hill, 1990) and passes through redoximorphic soil conditions (Hedin et al., 1998; Bohlke et al., 2002).

Even though substantial denitrification rates have been measured in riparian zones, the extent and nature of denitrification in these areas is still highly uncertain. Several studies suggest that some riparian zones do not significantly reduce groundwater  $\text{NO}_3^-$  concentrations (Bohlke and Denver, 1995; Pinay et al., 1998; Puckett et al., 2002; Puckett and Hughes, 2005). If the riparian zone does not have a shallow aquaclude, groundwater will flow under the biologically active zone, plants will not be able to immobilize N, and  $\text{NO}_3^-$  will leach into nearby surface waters (Cey et al., 1999; Hill et al., 2000). In addition, short groundwater residence times allow for oxic conditions to exist, resulting in unfavorable conditions for denitrification. Nitrate is then passively carried by groundwater and leached into nearby surface water. Low DOC concentrations also hinder denitrification resulting in relatively constant groundwater  $\text{NO}_3^-$  concentrations (Hill et al., 2000). Finally, denitrification can occur upslope from the riparian zone, in which case relatively low groundwater  $\text{NO}_3^-$  concentrations in the riparian zone might be misinterpreted as denitrification.

van Breemen et al. (2002) constructed N budgets for sixteen large watersheds in the northeastern United States. Denitrification in terrestrial soils was the most uncertain estimate and was estimated by the difference between all

N inputs and the sum of measured loss terms and biomass storage. Fluxes of N loss as a result of denitrification are difficult to estimate because the control mechanisms of denitrification in the field situation are not well understood, despite extensive knowledge of the fundamental microbiology.

Because nutrient cycles and groundwater chemical composition in riparian groundwater are influenced by hydrogeomorphic characteristics, it is essential to examine hydrologic parameters and dynamics (Phillips et al., 1993; Hamilton and Helsel, 1995; Puckett, 2004). The ease with which a liquid flows through a porous medium, known as hydraulic conductivity, is affected by soil composition and grain size (Schwartz and Zhang, 2003). Heterogeneous geologic units consisting of many different hydraulic conductivities create complex hydrologic flow paths. Nutrients in groundwater flowing through soil layers with higher hydraulic conductivities have a greater chance of being carried to nearby surface water. Dilution of dissolved nutrients is affected by physical properties such as advection and dispersion. Davis (1969) observed groundwater flow in bedded sediment showed greater permeability along a sediment layer compared to groundwater flow between sediment layers. Microbial processes or plant uptake both can influence nutrient concentrations in shallow groundwater flowing through soils with low to moderate hydraulic conductivities. In general, as groundwater flows through the soil or as the groundwater table rises, ions and DOC can be mobilized within the soil (Boyer et al., 2000).

Another example of hydrogeomorphic factors influencing  $\text{NO}_3^-$  concentrations are confining soil layers, known as aquicludes. A shallow

aquiclude is needed to force the groundwater to flow within the shallow root layer and the biologically active riparian habitats containing organic C. The aquiclude then facilitates reduction of groundwater N concentrations by microbial immobilization, plant uptake, and denitrification (Jacobs and Gilliam, 1985; Cooper, 1990; Jordan et al., 1993; Cey et al., 1999; Hill et al., 2000). Uptake of N by plant roots located within the biologically active riparian habitats can immobilize N temporarily. This can result in deciduous leaf litter containing a significant pool of N and during leaf senescence, N is cycled back into the forest soil as organic N. Nitrogen species that are not immobilized by abiotic and biotic processes are leached into groundwater.

An important soil characterization, cation exchange capacity (CEC), describes the amount of exchangeable cations per unit weight of dry soil. Cation exchange influences groundwater chemistry as well as alters soil physical properties. Ions with a lower charge will replace those ions with a higher charge within the major structural layers of the soil. In most temperate soils, a net negative charge exists due to the 2:1 clays and accumulation of soil organic matter. Thus, cation exchange is more likely to occur than anion exchange (Miller and Donahue, 2001). Soil CEC can influence groundwater cation concentrations in temperate soils.

### **Overall Objective**

Even though there is a vast amount of literature examining riparian denitrification, examination of many different riparian factors is essential to fully understanding N loss, controls on denitrification rates, and improve riparian

ecosystem management. Studying denitrification rates in a riparian zone in a northeastern suburban coastal watershed where N inputs are typically high will provide insight for riparian ecosystem dynamics and management. For this study, a riparian zone was chosen in the suburban Oyster River watershed located in coastal New Hampshire.

The main objectives were to: 1) characterize groundwater elevation and flow path as well as groundwater dissolved oxygen (DO), nitrate ( $\text{NO}_3^-$ ), ammonium ( $\text{NH}_4^+$ ), total dissolved nitrogen (TDN), dissolved organic carbon (DOC), and sulfate ( $\text{SO}_4^{2-}$ ) to determine if they indicate an N loss due to denitrification; 2) determine if denitrification is occurring through field experimentation using the “push-pull” method; and 3) determine if  $\text{NO}_3^-$  and DOC quantity control rates of denitrification. I hypothesized that 1) the physical and chemical constituents in ambient groundwater do indicate N loss from denitrification; 2) denitrification will occur during push-pull tests; and 3)  $\text{NO}_3^-$  and DOC quantity will influence denitrification rates.

## CHAPTER I

### RESEARCH METHODS

#### **Site Description**

The Oyster River watershed is located in coastal New Hampshire. A housing development, known as James Farm, is located on the border of the Oyster and Lamprey River watersheds in Lee, New Hampshire. A conservation area located in James Farm contains a groundwater well field located within a riparian zone (Figure 1). The well field is approximately 18.5 m<sup>2</sup> and the location is 43°07'44.47"N Latitude and 70°59'31.75"N Longitude. The total annual precipitation for 2005 and 2006 was 124 cm and 155 cm, respectively. Corresponding values for autumn only were 18 cm and 14 cm. The mean annual temperatures for 2005 and 2006 were 8.1°C and 10.11°C, respectively. Corresponding values for autumn only were 10.6°C and 10.3°C.

A stream runs along side the well field, which flows into James Farm Fire Pond. The pond acts as a surface- and groundwater output from the well site. The topography is shallow with minor relief. The well field soil type is part of the Presumpscott Formation, which includes sediments ranging from silty to sandy clay (Rolfs et al., 1996). The James Farm well field contains well drained soils on the uplands, and some poorly drained soils formed by marine deposits of silt and clay in more low-lying areas, as well as areas with very sandy soils (Soil Conservation Service, 1973). The stream substrate is primarily sand. There is a



confining clay layer located at a depth of approximately 1.5 m. The well field is located in a deciduous forest containing red maple (*Acer rubrum*), oak (*Quercus spp.*), American elm (*Ulmus americana*), white ash (*Fraxinus americana*), birch (*Betula spp.*), and ironwood (*Carpinus caroliniana*). The ground vegetation consists of cinnamon fern (*Osmunda cinnamomea*), starflower (*Trientalis borealis*), Canada mayflower (*Maianthemum canadense*), and false solomon's seal (*Smilacina racemosa*).

To observe riparian groundwater constituent dynamics, the James Farm riparian well field contains fourteen 5.08 cm diameter polyvinyl chloride wells (Figure 1). The wells were used to examine monthly nutrient dynamics and were labeled A1-A5, A7-A13, A-01 and A-02. The depth to the water table (DTWT) was the only parameter measured for wells A-01 and A-02. A metal staff in the stream close to A3 represents the stream sampling location. The wells used for the push-pull method were A1, A11, A12, and A3. The four wells were chosen because they had differences in groundwater elevations, different ambient groundwater  $\text{NO}_3^-$  and DOC concentrations, and hydraulic conductivities that should promote denitrification as well as conducive to the push-pull method. The wells were installed using a hand auger to depths approximately 1 m below the groundwater table. Wells A1-A5, A7, and A8 were installed in the summer of 1995, A9-A11 and JF-Staff in August, 2004, A-01 and A-02 in May, 2005, and A12 and A13 were installed on 19 November, 2004. The perforated length of the well casing was 53 cm for A1 and A3, 61 cm for A11, and 76 cm for A12.

Detailed soil profiles were previously recorded for A1 and A3 whereas soil

profiles for A11 and A12 were estimated using soil profiles from wells A6 and A7, respectively (Table 1). The screened portion of the wells intercepted 5-10 different soil compositions ranging from sand to clay. The screened lengths of the wells were 53 cm, 61 cm, or 76 cm and ranged from 20 to 90 cm below the soil surface. The depths from the soil surface to an aquitard for A1, A11, A12, and A3 were 109 cm, 45 cm, 55 cm, and 122 cm, respectively.

### **Hydrologic Characteristics**

Observing groundwater table dynamics was essential to determine hydrological characteristics within the well field. To determine monthly groundwater table elevations, relative well casing heights were established and DTWT from the top of each well casing was measured monthly. Relative well heights were surveyed to a common datum on 20 September, 2004 and 7 September, 2005. The datum was determined by an arbitrary height above the soil surface.

Distinctive topographic features were also surveyed. The direction of groundwater flow was estimated by monthly groundwater table elevations. The groundwater elevation, known as hydraulic head, mimicked topography with higher hydraulic head in the middle of the well field and lower hydraulic head on the East and West sides of the well field. James Farm DTWT measurements began 27 July, 2004 for A1 and A3 while A12 and A13 DTWT measurements began 8 December, 2004.

Groundwater residence time at each well was estimated by calculating hydraulic conductivities from slug test data. The slug tests were conducted once

during June 2006 using a Solinst Levellogger pressure transducer, which measured hydraulic head every second. The volume of the slug was 309 mL. The hydraulic conductivities were determined by the Hvorslev's equation (Schwartz and Zhang, 2003):

$$K = (R^2)/(2L(t_2 - t_1) \ln(L/R) \ln(H_1/H_2))$$

where R is the radius of the well casing, L is the perforated length of the well casing, and  $t_1$  and  $t_2$  is the time at a specific hydraulic head ( $H_1$ ,  $H_2$ ). The hydraulic conductivities ranged from  $10^{-3}$  to  $10^{-5}$  cm sec<sup>-1</sup> (Table 2).

### **Monthly Groundwater Collection and Analysis**

Groundwater samples were collected monthly from July 2004 until August 2006. Groundwater was bailed out of each well until no water remained or stopped after ten repetitions of water removal. After groundwater recharge, an acid washed 250 mL high density polyethylene (HDPE) Nalgene bottle was rinsed 3 times with well water before filling the bottle completely with groundwater. Samples were filtered within 24 hours after the collection time using a precombusted (425°C for 4-6 hours) 0.7 µm glass fiber filter into a 60 mL HDPE bottle and frozen until further analysis. All sample bottles were acid washed with dilute HCl followed by six rinses with deionized water. After sample collection, groundwater pH, temperature (°C), specific conductivity (EC), and dissolved oxygen (DO) were measured with a YSI 556 meter in each well.

Samples were analyzed in the Water Resources Research Center

(WRRRC) laboratory at the University of New Hampshire. Ammonium ( $\text{NH}_4^+$ ) was analyzed using a Smartchem discrete analyzer using the automated phenate method (US EPA method 350.1). Silica ( $\text{SiO}_2$ ) was analyzed using a Smartchem discrete analyzer using the automated molybdate reactive method (Greenberg, 1992). Dissolved organic carbon (DOC) (measured as non-purgeable organic carbon) was analyzed by a Shimadzu TOC-5000 with an ASI-5000 autosampler using high temperature catalytic oxidation (HTCO) (US EPA method 415.1), while total dissolved nitrogen (TDN) was analyzed by HTCO with an Antek 720C Chemiluminescent N detector (Merriam et al, 1996). Anions ( $\text{NO}_3^-$ ,  $\text{Br}^-$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$ ) and cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$ ) were measured using a Waters ion chromatograph. Anions were measured via Dionex micromembrane suppressed ion chromatography, while cations were measured directly (US EPA method 300.1).

### **In Situ Push-Pull Tests**

In situ  $\text{NO}_3^-$  push-pull tests and glucose push-pull tests were conducted in four groundwater wells (A1, A11, A12, and A3). The single well, push-pull test method quantifies groundwater denitrification in discrete riparian zone areas (Trudell et al., 1986; Istok et al., 1997; Addy et al., 2002). The  $\text{Br}^-$  and  $\text{NO}_3^-$  push-pull tests began 5 September, 2006 and ended on 17 September, 2006, the low  $\text{NO}_3^-$  and glucose push-pull tests began on 16 September, 2006 and ended on 28 September, 2006, and the high  $\text{NO}_3^-$  and glucose push-pull tests began on 22 October, 2006 and ended on 10 November, 2006.

For each push-pull groundwater well, ambient concentrations of  $\text{NO}_3^-$ ,

$\text{NH}_4^+$ , TDN, DOC,  $\text{Br}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{SiO}_2$  were measured during three consecutive days prior to the push-pull tests. There were three push-pull tests conducted in each well. During the first push-pull test, known as the  $\text{Br}^-$  and  $\text{NO}_3^-$  addition, bromide ( $\text{NaBr}$ ) and nitrate ( $\text{NaNO}_3$ ) were added to 11 L of groundwater collected from the experimental well and other wells with similar groundwater chemistry into a Nalgene carboy (Table 3). Groundwater was used from other wells because not enough groundwater could be extracted from the specific addition well being examined. During the 2<sup>nd</sup> push-pull test, known as the 1<sup>st</sup> glucose addition,  $\text{NaBr}$ ,  $\text{NaNO}_3$ , and dissolved organic carbon (dextrose) were added to the 11 L groundwater solution and vigorously mixed (Table 3). During the 3<sup>rd</sup> push-pull test, known as the 2<sup>nd</sup> glucose addition, larger amounts of  $\text{NaBr}$ ,  $\text{NaNO}_3$ , and dextrose were mixed in to the 11 L groundwater solution (Table 3). To reduce DO to ambient levels, helium was bubbled through the groundwater solution (approximately 20 minutes per solution). Approximately 10 L of the groundwater solution was pumped back into the well, known as the push phase, with a peristaltic pump fitted with plastic tubing for approximately 20 to 60 minutes depending on how quickly the groundwater solution was exiting the groundwater well and into surrounding soil. Ten L of water occupies approximately 44 kg of dry soil, resulting in an estimated initial plume of 15 to 30 cm diameter. Groundwater samples were collected into 125 mL acid washed HDPE bottles using the peristaltic pump at periodic intervals throughout the push phase and throughout the 7 days after the 10 L was pumped into the well, known as the pull phase. A sample was taken from approximately 1 L of the solution

remaining in the carboy once 10 L was pushed into the well to determine if chemical concentrations remained similar throughout the push phase. Each groundwater sample was taken from the middle of the screened portion of the well.

Recovery of the  $\text{Br}^-$  tracer was used to determine the rate at which the introduced plume exited the screened portion of the well. A series of calculations was used to determine the  $\text{Br}^-$  tracer recovery rates and if  $\text{NO}_3^-$  and DOC diluted at the same rate as  $\text{Br}^-$ . The rate at which the added  $\text{Br}^-$  concentrations decreased was calculated by the following equation:

$$1 - (\text{Br}_x - \text{Br}_{\text{amb}}) / (\text{Br}_{\text{start}} - \text{Br}_{\text{amb}}) \quad (\text{Eq. 1})$$

where  $\text{Br}_x$  is the bromide concentration at time x,  $\text{Br}_{\text{amb}}$  is the ambient bromide concentration, and  $\text{Br}_{\text{start}}$  is the bromide concentration at time 0, known as the first sample collected directly after the push phase. Once the 10 L of groundwater solution containing  $\text{Br}^-$  and  $\text{NO}_3^-$  was added to the well, the rate at which added  $\text{NO}_3^-$  concentrations decreased was determined by the following equation:

$$\text{NO}_3^-_{\text{start}} * (\text{Br}_x - \text{Br}_{\text{amb}}) / (\text{Br}_{\text{start}} - \text{Br}_{\text{amb}}) \quad (\text{Eq. 2})$$

where  $\text{NO}_3^-_{\text{start}}$  is the nitrate concentration at time 0. The incoming ambient groundwater  $\text{NO}_3^-$  concentrations can be defined as

$$(1 - (\text{Br}_x - \text{Br}_{\text{amb}}) / (\text{Br}_{\text{start}} - \text{Br}_{\text{amb}})) * \text{NO}_3^-_{\text{amb}} \quad (\text{Eq. 3})$$

where  $\text{NO}_3^-_{\text{amb}}$  is the ambient  $\text{NO}_3^-$  concentration. The sum of Eq. (2) and Eq. (3) determined what the  $\text{NO}_3^-$  concentration would be in the well if the only influence on  $\text{NO}_3^-$  concentrations was dilution.

$$\text{NO}_3^- \text{ start} * (\text{Br}_x - \text{Br}_{\text{amb}}) / (\text{Br}_{\text{start}} - \text{Br}_{\text{amb}}) + (1 - (\text{Br}_x - \text{Br}_{\text{amb}}) / (\text{Br}_{\text{start}} - \text{Br}_{\text{amb}})) * \text{NO}_3^- \text{ amb} \quad (\text{Eq. 4})$$

The difference of the  $\text{NO}_3^-$  concentration at time x and Eq. (4) determines if  $\text{NO}_3^-$  is decreasing or increasing relative to dilution calculated with the  $\text{Br}^-$  tracer. The same equations were used when determining DOC and  $\text{Na}^+$  loss or production. Nitrate loss describes  $\text{NO}_3^-$  decreasing faster than added  $\text{Br}^-$  concentrations over time. Nitrate production describes an increased  $\text{NO}_3^-$  concentration compared to what  $\text{NO}_3^-$  would be if only dilution was occurring. The same description applies to DOC and  $\text{Na}^+$  loss and production. Low incoming ambient  $\text{Br}^-$  concentrations in the addition wells ( $x = 0.05 \text{ mg L}^{-1}$ ) were taken into account when calculating loss and production terms.

### **Statistical Analyses**

The software package JMP (Version 7.0) was used to perform statistical analyses. A repeated measures oneway analysis of variance was used to determine differences ( $\alpha=0.05$ ) of  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , and DOC by year and by well. A oneway analysis of variance using a post-hoc Tukey test was performed to determine if mean  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , and DOC concentrations from the entire sampling period varied between wells.

## CHAPTER II

### RESULTS

#### **Hydrologic Characteristics**

The groundwater table demonstrated seasonal trends, with hydraulic head highest during the winter and late spring and lowest during the late summer and early autumn. However, the general groundwater flow path remained similar throughout the year. A substantial increase in hydraulic head occurred from September, 2005 through November, 2005 and remained higher compared to groundwater tables in 2004-2005. Throughout the sample period, the groundwater table was dynamic with the largest and smallest fluctuations of hydraulic head occurring in A11 (0.65 m) and A13 (0.16 m) (Figure 2). The largest and smallest fluctuation in hydraulic head for autumn 2005 was 0.5 m (A3) and 0.02 m (A4), respectively. The groundwater table relative to the soil surface during autumn 2005 for A1, A11, A12, and A3 were 0.16 m, 0.13 m, 0.13 m, and 0.09 m, respectively. The distance from the average autumn 2005 water table down to the middle of the screened portion of A1, A3, A11, and A12 was 0.74 m, 1.03 m, 0.32 m, and 1.03 m, respectively.

#### **Monthly Samples**

All wells followed seasonal patterns of increasing DO concentrations during the autumn and winter and decreasing concentrations during the spring and summer. Generally, DO did not demonstrate spatial trends (Table 4). All



wells remained oxic throughout the sampling period although A5 and A8 during the spring and early summer did decline to levels of  $<3 \text{ mg L}^{-1}$  and  $4 \text{ mg L}^{-1}$ , respectively. Mean groundwater temperature (approximately  $10^{\circ}\text{C}$ ) increased as it flowed through the well field (Table 4). There were no seasonal or spatial trends in EC in all wells except at A11 where EC increased during the summer (Table 4). The EC means ranged from  $300 \mu\text{S cm}^{-1}$  to  $463 \mu\text{S cm}^{-1}$ . There were no seasonal or spatial pH trends in all wells and the means ranged from 6.75 to 7.28 (Table 4).

A3 mimicked stream temperature, DO, and EC temporal patterns. However, A3 temperature and EC were higher and DO was lower compared to the stream. Other wells close to the stream (A10 and A11) did not mimic stream temporal patterns or mean concentrations of physical properties except for a similar mean pH in A10 and JF-Staff (7.22 and 7.18, respectively).

There were no clear seasonal  $\text{NO}_3^-$  patterns for any wells except that  $\text{NO}_3^-$  increased in the summer for A8 and JF-Staff. In general, wells located in the North and Southwest areas of the well field had higher mean  $\text{NO}_3^-$  and wells located in the center of the well field had lower mean  $\text{NO}_3^-$  concentrations (Figure 3). Mean  $\text{NO}_3^-$  combining all wells was  $<2.4 \text{ mg N L}^{-1}$  (Table 4). A4 and A7 were the only wells with a significant increase in  $\text{NO}_3^-$  concentrations from 1995 to 2006 ( $p<0.05$ ). Overall, there were significant differences in mean  $\text{NO}_3^-$  in the James Farm wells ( $p<0.05$ ) (Table 5).

There was an inverse relationship between  $\text{NO}_3^-$  and DOC for all wells with stronger inverse relationships in A1, A5, A7, A10, A11, and JF-Staff (Figure

4). Mean DOC combining all wells was  $<2.7 \text{ mg C L}^{-1}$  (Table 4). In general, mean DOC decreased in all wells from 2004 to 2006 with significant decreases occurring in A1, A2, A4, A7, A10, A12, and A13 ( $p<0.05$ ) (Table 6, Figure 5). Mean DOC was significantly different in the James Farm wells ( $p<0.05$ ) (Table 6). In general, wells located in the North and Southwest areas of the well field had lower mean DOC, while wells in the center of the well field had higher mean DOC (Table 4).

Sulfate and  $\text{SiO}_2$  demonstrated seasonal trends. Sulfate increased in each well and in the stream during the spring and summer except for A5 and A9. In general,  $\text{SiO}_2$  concentrations increased during the summer and early autumn and decreased in the winter in all wells and in the stream. Mean  $\text{SO}_4^{2-}$  and  $\text{SiO}_2$  were  $<5 \text{ mg L}^{-1}$  and  $<19 \text{ mg L}^{-1}$ , respectively (Table 7). Two wells in the middle of the well field (A5 and A8) had the lowest mean  $\text{SO}_4^{2-}$ . Other wells located throughout the middle of the well field had similar  $\text{SO}_4^{2-}$  concentrations compared to wells on the outer edges of the well field (Table 7). Sulfate in all wells slightly increased from 2004 to 2006 except A8 and A9 (Figure 6). All wells had low  $\text{SO}_4^{2-}$  concentrations with low  $\text{NO}_3^-$  concentrations except for A2, A3, and A12. Silica concentrations decreased from 2004 to 2006 except for A1, A12, A13, and JF-Staff (Figure 7). Silica did not show spatial trends in the well field (Table 7).

There were no seasonal or spatial trends of  $\text{NH}_4^+$ ,  $\text{Br}^-$ ,  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  in the wells. The well field groundwater was high in  $\text{Cl}^-$  ( $53 \text{ mg L}^{-1}$ ),  $\text{Na}^+$  ( $15 \text{ mg L}^{-1}$ ),  $\text{Ca}^{2+}$  ( $25 \text{ mg L}^{-1}$ ), and  $\text{Mg}^{2+}$  ( $11 \text{ mg L}^{-1}$ ) and low in  $\text{NH}_4^+$  ( $39 \text{ } \mu\text{g N L}^{-1}$ ),  $\text{Br}^-$  ( $0.05 \text{ mg L}^{-1}$ ), and  $\text{K}^+$  ( $1.45 \text{ mg L}^{-1}$ ) (Table 4 and 7). Ammonium

concentrations generally increased beginning in November, 2005 to August, 2006 in A1, A2, A3, A5, A8, A11, A12, and JF-Staff (Figure 8). A5 was the only well with significantly different mean  $\text{NH}_4^+$  as well as a significant increase of mean  $\text{NH}_4^+$  from 1995 to 2006 ( $p < 0.05$ ). Mean  $\text{Br}^-$  was at or below the detection limit ( $0.04 \text{ mg L}^{-1}$ ) in A1, A4, A8, A10, A11, and JF-Staff. All other wells had  $\text{Br}^-$  concentrations of  $< 0.13 \text{ mg L}^{-1}$ . Other ions ( $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ ) demonstrated variable concentrations throughout the sampling period (Table 7).

### **In Situ Push-Pull Tests**

The push-pull  $\text{Br}^-$  tracer recovery rates showed added  $\text{Br}^-$  exiting the well similarly for A1 and A3 for each addition, while  $\text{Br}^-$  decreased more quickly with each consecutive addition for A12 and A11 (Figure 9). Relatively low  $\text{NO}_3^-$  concentrations were added during the  $\text{Br}^-$  and  $\text{NO}_3^-$  addition and the 1<sup>st</sup> glucose addition, while large amounts of  $\text{NO}_3^-$  were added for the 2<sup>nd</sup> glucose addition (Figure 10). Low DOC concentrations were added for the 1<sup>st</sup> glucose addition, while large amounts of DOC were added for the 2<sup>nd</sup> glucose addition (Figure 11 and 12).

### **$\text{NO}_3^-$ Loss and Production Trends**

#### **$\text{Br}^-$ and $\text{NO}_3^-$ Addition**

During the  $\text{Br}^-$  and  $\text{NO}_3^-$  push-pull tests,  $\text{NO}_3^-$  loss occurred in A1 and A3,  $\text{NO}_3^-$  loss and production occurred in A11, and slight  $\text{NO}_3^-$  production occurred in A12 (Figure 13). A steep  $\text{NO}_3^-$  loss occurred in A1 after 30 min of immediate  $\text{NO}_3^-$  production following the push phase. A11  $\text{NO}_3^-$  loss began immediately after the push phase. Nitrate production began in A11 after day 1 through day 7.

Nitrate loss occurred in A3 throughout the entire pull phase. A slight  $\text{NO}_3^-$  production occurred for A12 from day 2 through day 5.

#### 1<sup>st</sup> Glucose Addition

Nitrate loss occurred in each well during the 1<sup>st</sup> glucose additions (Figure 15). The largest  $\text{NO}_3^-$  losses occurred in A1 and A11 (Figure 13). Nitrate loss in A1 slowly began to decrease 4 hours after the push phase. The largest  $\text{NO}_3^-$  loss in A11 occurred on day 3 of the pull phase. A gradual  $\text{NO}_3^-$  loss in A12 occurred throughout the pull phase (Figure 13). Nitrate loss in A3 remained around  $0.04 \text{ mg N L}^{-1}$  throughout the pull phase (Figure 13).

#### 2<sup>nd</sup> Glucose Addition

In general,  $\text{NO}_3^-$  loss was observed in A11, A12, and A3, while  $\text{NO}_3^-$  production was observed in A1 (Figure 13). Nitrate production in A1 occurred throughout the majority of the pull phase. Slight  $\text{NO}_3^-$  loss in A1 occurred during day 1 and the highest  $\text{NO}_3^-$  production occurred on day 2. Nitrate loss and production in A11 occurred through day 1, while a steep  $\text{NO}_3^-$  loss began on day 2. A12 and A3 had slight  $\text{NO}_3^-$  loss throughout the pull phase.

### **DOC Loss and Production Trends**

#### $\text{Br}^-$ and $\text{NO}_3^-$ Addition

Dissolved organic carbon concentrations increased from average ambient concentrations by as much as  $3.2 \text{ mg C L}^{-1}$  in A1 and  $4.02 \text{ mg C L}^{-1}$  in A11 during day 1, then DOC began to decrease on day 2 (Figure 11 and 14). Dissolved organic carbon slightly increased by  $0.64 \text{ mg C L}^{-1}$  in A12 through day 2 and  $0.33 \text{ mg C L}^{-1}$  in A3 through day 1 (Figure 11 and 14). Increased DOC concentrations

resulted in DOC production.

#### 1<sup>st</sup> Glucose Addition

Dissolved organic carbon production occurred in A11 and A1 (Figure 14). A11 DOC production was the highest compared to the other wells (Figure 14). A1 DOC production occurred throughout the pull phase with the largest DOC production occurring approximately 7 hours after the push phase (Figure 14). Variable DOC loss and production occurred in A12 and A3 throughout the pull phase (Figure 14). A12 had maximum DOC production on day 2 while A3 had maximum DOC production occur during the first 1.5 hours after the pull phase.

#### 2<sup>nd</sup> Glucose Addition

Immediate DOC production occurred in A11 and A12 while immediate DOC loss occurred in A1 and A3 during the first 30 min of the pull phase (Figure 14). Then, throughout the afternoon of day 1 and continuing for the duration of the pull phase, there was a slight continuous DOC loss for A1 and A12 (Figure 14). A3 had a larger immediate DOC loss, which slowed to minimal DOC loss by day 2. A11 had the largest DOC loss compared to the other wells, which lasted from day 1 through day 4 with a maximum loss of  $17.6 \text{ mg C L}^{-1}$  occurring on day 1 while DOC production occurred on day 5.

### **Precipitation Events**

#### Br<sup>-</sup> and NO<sub>3</sub><sup>-</sup> Addition

One rain event occurred during the Br<sup>-</sup> and NO<sub>3</sub><sup>-</sup> additions on 14 September, 2006 (Table 8). The precipitation NO<sub>3</sub><sup>-</sup> concentration was lower than the added NO<sub>3</sub><sup>-</sup> in the wells. A11, A1, and A3 additions ended before the rain

event. The only well where  $\text{NO}_3^-$  concentrations decreased was A12 ( $0.04 \text{ mg N L}^{-1}$ ). The precipitation DOC concentration from the rain event was  $0.63 \text{ mg C L}^{-1}$ . A12 DOC concentrations increased  $0.09 \text{ mg C L}^{-1}$ .

#### 1<sup>st</sup> Glucose Addition

The two large rain events occurred on 19 September, 2006 and 20 September, 2006 during the 1<sup>st</sup> glucose additions (Table 8). Precipitation  $\text{NO}_3^-$  concentrations during the two rain events were  $0.27 \text{ mg N L}^{-1}$  and  $0.75 \text{ mg N L}^{-1}$ , respectively. A12, A1, and A3 groundwater  $\text{NO}_3^-$  did not increase after one day of each rain event, however A11 groundwater  $\text{NO}_3^-$  concentrations decreased  $0.66 \text{ mg N L}^{-1}$ . Precipitation DOC concentrations during the two rain events were  $1.65 \text{ mg C L}^{-1}$  and  $1.43 \text{ mg C L}^{-1}$ , respectively. Groundwater DOC concentrations in A11 increased  $1.51 \text{ mg C L}^{-1}$  and  $1.43 \text{ mg C L}^{-1}$  and A3 groundwater DOC concentrations increased  $0.03 \text{ mg C L}^{-1}$  for both rain events. A12 and A1 groundwater DOC concentrations decreased during the 20 September, 2006 rain event by  $0.15 \text{ mg C L}^{-1}$  and  $0.58 \text{ mg C L}^{-1}$ , respectively. A12 and A1 1<sup>st</sup> glucose additions did not begin before the 20 September, 2006 rain event.

#### 2<sup>nd</sup> Glucose Addition

There were four large rain events during the 2<sup>nd</sup> glucose additions. Precipitation  $\text{NO}_3^-$  concentrations during rain events ranged from  $0.04 \text{ mg N L}^{-1}$  to  $0.68 \text{ mg N L}^{-1}$  (Table 8). A12 was the only well with increasing  $\text{NO}_3^-$  concentrations from the 3 November, 2006 rain event ( $0.09 \text{ mg N L}^{-1}$ ). A11  $\text{NO}_3^-$  concentrations decreased  $0.14 \text{ mg N L}^{-1}$  and  $0.91 \text{ mg N L}^{-1}$  during the first two

rain events. A12 and A1  $\text{NO}_3^-$  production occurred during the rain event on 9 November, 2006. Precipitation DOC concentrations ranged from 0.2  $\text{mg C L}^{-1}$  to 0.95  $\text{mg C L}^{-1}$  (Table 8). A12 was the only well with increasing DOC concentrations from any 2<sup>nd</sup> glucose addition rain event (0.18  $\text{mg C L}^{-1}$ ). In general,  $\text{NO}_3^-$  and DOC concentrations changed slightly in some wells during different rain events, but consistent concentration changes in all wells for each rain event did not occur.

### **Trends in Physical Constituents during Push-Pull Tests**

Dissolved oxygen (DO) concentrations during all of the additions ranged from 0.83  $\text{mg L}^{-1}$  to 8.04  $\text{mg L}^{-1}$ . Mean DO for the  $\text{Br}^-$  and  $\text{NO}_3^-$  addition and 1<sup>st</sup> glucose addition was 4.74  $\text{mg L}^{-1}$  and 4.28  $\text{mg L}^{-1}$ , respectively, while mean DO during the 2<sup>nd</sup> glucose addition was 5.81  $\text{mg L}^{-1}$  (Figure 15). A11 was the only well that approached anoxic conditions ( $<3 \text{ mg L}^{-1}$ ) during the push-pull tests, which occurred during the  $\text{Br}^-$  and  $\text{NO}_3^-$  addition and the 1<sup>st</sup> glucose addition. Groundwater temperature for all additions for all wells increased during day 1 and then decreased to ambient temperatures for the duration of each addition (Figure 16). Mean temperatures were similar for the  $\text{Br}^-$  and  $\text{NO}_3^-$  addition and 1<sup>st</sup> glucose addition (14.44°C and 14.33°C, respectively). However, mean temperature for the 2<sup>nd</sup> glucose addition was 9.7°C. The variance in EC was the highest in all wells during the 2<sup>nd</sup> glucose addition except A1 (Figure 17). There were no spatial trends of EC over time when comparing each well during the same addition. The pH was variable ranging from 5.94 to 7.96 throughout the additions and generally pH increased immediately following the push phase for

all additions in all wells (Figure 18). Generally, A1 and A12 pH trends over time were similar for each addition. A11 pH decreased from day 1 to day 2 for all additions. During the  $\text{Br}^-$  and  $\text{NO}_3^-$  addition, A11 pH generally increased from day 2 through day 7, however pH generally decreased through day 7 during the 1<sup>st</sup> glucose addition and 2<sup>nd</sup> glucose addition.

### **Push-Pull Ion Trends**

Ammonium concentrations ( $\mu\text{g N L}^{-1}$ ) did not have any distinct temporal trends for each well for each addition (Figure 19). Ammonium concentrations in A1 were the most variable compared to the other wells with the highest range occurring throughout the  $\text{Br}^-$  and  $\text{NO}_3^-$  addition (3 to  $59 \mu\text{g N L}^{-1}$ ). A11  $\text{NH}_4^+$  concentrations were the most variable during the  $\text{Br}^-$  and  $\text{NO}_3^-$  addition (0 to  $38 \mu\text{g N L}^{-1}$ ). A12 and A3 had the most variable  $\text{NH}_4^+$  concentrations during the 1<sup>st</sup> glucose addition ranging from 0 to  $40 \mu\text{g N L}^{-1}$  and 4 to  $42 \mu\text{g N L}^{-1}$ , respectively.

Overall,  $\text{SO}_4^{2-}$  concentrations were the highest during the  $\text{Br}^-$  and  $\text{NO}_3^-$  additions and lowest during the 2<sup>nd</sup> glucose additions in all wells except A3 (Figure 20). During the  $\text{Br}^-$  and  $\text{NO}_3^-$  additions,  $\text{SO}_4^{2-}$  concentrations increased relative to ambient concentrations from  $0.45 \text{ mg L}^{-1}$  to  $0.66 \text{ mg L}^{-1}$  for all wells. During the 1<sup>st</sup> glucose additions, A1 and A3  $\text{SO}_4^{2-}$  concentrations increased by approximately  $0.30 \text{ mg L}^{-1}$  (Figure 20). Meanwhile, throughout the 1<sup>st</sup> glucose additions A11 and A12  $\text{SO}_4^{2-}$  concentrations remained relatively similar compared to ambient concentrations. During the 2<sup>nd</sup> glucose additions,  $\text{SO}_4^{2-}$  concentrations increased about  $0.4 \text{ mg L}^{-1}$  for A1, A12, and A3 during day 1 of the pull phase (Figure 20). A11  $\text{SO}_4^{2-}$  concentrations increased  $0.45 \text{ mg L}^{-1}$  from



ambient concentrations immediately following the push phase. The only instance where  $\text{SO}_4^{2-}$  concentrations decreased below ambient concentrations was in A11 on day 5 during the 2<sup>nd</sup> glucose addition ( $1.51 \text{ mg L}^{-1}$ ).

Because  $\text{Na}^+$  was added as NaBr and  $\text{NaNO}_3$ ,  $\text{Na}^+$  loss and production trends were calculated the same as  $\text{NO}_3^-$  and DOC loss and production trends. Sodium recovery rates did not Br<sup>-</sup> recovery rates (Figure 21). Ambient  $\text{Na}^+$  concentrations measured 3 days prior to the additions ranged from  $12 \text{ mg L}^{-1}$  to  $18 \text{ mg L}^{-1}$ . Sodium concentrations for all wells for all additions ranged from  $9 \text{ mg L}^{-1}$  to  $29 \text{ mg L}^{-1}$ . Sodium production occurred for all wells during the Br<sup>-</sup> and  $\text{NO}_3^-$  addition. During the 1<sup>st</sup> glucose addition, there was a slight  $\text{Na}^+$  production for A1 from the end of day 1 through day 5,  $\text{Na}^+$  loss occurred in A11 and A12, and A3  $\text{Na}^+$  concentrations generally diluted away (Figure 21). Sodium loss occurred during the 2<sup>nd</sup> glucose additions in A11 and A3 even though an increased amount of NaBr and  $\text{NaNO}_3$  was added during the 2<sup>nd</sup> glucose push phase (Figure 21). A12 and A1 had variable  $\text{Na}^+$  loss and production through the pull phase.

There were a few trends between cations and added DOC and  $\text{Na}^+$ . Throughout the Br<sup>-</sup> and  $\text{NO}_3^-$  addition, A1, A11, and A12  $\text{K}^+$  concentrations and DOC loss and production trends were similar. Throughout the 1<sup>st</sup> glucose addition, A11  $\text{K}^+$  concentrations and Na loss and production trends followed opposite patterns. Throughout the 1<sup>st</sup> glucose addition and 2<sup>nd</sup> glucose addition, A11  $\text{Mg}^{2+}$  concentrations and  $\text{Na}^+$  loss and production trends were similar. During day 1 of the 1<sup>st</sup> glucose addition, A12 and A11  $\text{Ca}^{2+}$  concentrations

increased while  $\text{Na}^+$  loss increased. A11 DOC and  $\text{K}^+$  concentrations increased while  $\text{Na}^+$  loss increased during day 1 of the 1<sup>st</sup> glucose addition. Throughout the 1<sup>st</sup> glucose addition, A11  $\text{Mg}^{2+}$  concentrations and DOC loss and production trends followed opposite patterns. There were no other trends in the wells when comparing DOC and  $\text{Na}^+$  loss and production trends to  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$  concentrations.

## CHAPTER III

### DISCUSSION

#### **Monthly Physical and Chemical Constituents**

Monthly sample data suggest that denitrification occurred at my site, as  $\text{NO}_3^-$  concentrations decreased along the groundwater flowpath through the well field. Dissolved organic carbon concentrations remained relatively high in wells located in the middle of the James Farm well field and DO concentrations were relatively low. Both high DOC and low DO are conducive to denitrification. Furthermore, anoxic conditions in wells (e.g. A5) were associated with low mean  $\text{NO}_3^-$  concentrations, again suggesting denitrification. The lowest mean  $\text{SO}_4^{2-}$  was found in A5 and might be attributed to anoxic conditions resulting in  $\text{SO}_4^{2-}$  reduction.

#### **Push-Pull $\text{NO}_3^-$ and DOC Production**

Apparent production of  $\text{NO}_3^-$  and DOC occurred several times throughout the addition experiments. The hydrogeology of the James Farm well field could have been the major influence on groundwater chemical concentrations and dynamics and might have been responsible for this apparent production of solutes.

There could be several confounding factors that led to the observed  $\text{NO}_3^-$  and DOC production trends. One factor is diverse vertical hydraulic conductivities due to the vertical heterogeneity of the James Farm well field

soil. Nitrate and DOC concentrations could be higher in soils with relatively low hydraulic conductivity. During the pull phase, higher  $\text{NO}_3^-$  and DOC concentrations in the soil layers with low hydraulic conductivities could have had a greater influence on  $\text{NO}_3^-$  concentrations from day 2 through the rest of the pull phase. For example,  $\text{NO}_3^-$  production in A1 during the 2<sup>nd</sup> glucose addition could be a result of incoming, relatively higher  $\text{NO}_3^-$  concentrations from soils with low hydraulic conductivity. Nitrate production in A1 only during the 2<sup>nd</sup> glucose addition could be a result of added  $\text{NO}_3^-$  from the  $\text{Br}^-$  and  $\text{NO}_3^-$  addition and 1<sup>st</sup> glucose addition that had infiltrated and accumulated in the soil layers with low hydraulic conductivity. Apparent production of DOC during the 1<sup>st</sup> and 2<sup>nd</sup> glucose addition could also be the result of vertical heterogeneity in soils. Slow release of DOC from soils with low conductivity could have caused DOC production during the 1<sup>st</sup> glucose addition for A1, A3, and A11. The substantial increase in DOC concentrations in A1 and A11 through day 2 and day 3 respectively could have resulted from saturating the surrounding soil around the well with the 10 L of groundwater solution during the  $\text{Br}^-$  and  $\text{NO}_3^-$  addition push phase and releasing DOC adsorbed within the soil. Saturating the surrounding soil during the push phase for the 1<sup>st</sup> glucose additions for A1 and A11 could have increased the groundwater DOC concentrations as well, resulting in DOC production. This could also explain the similar, but less obvious DOC concentration patterns for A12 during the  $\text{Br}^-$  and  $\text{NO}_3^-$  addition and the 1<sup>st</sup> glucose addition.

Variability of incoming ambient  $\text{NO}_3^-$  and DOC concentrations could have

also caused  $\text{NO}_3^-$  and DOC production (Bohlke and Denver, 1995). Nitrate loss in A1 and A12 was highest during the 1<sup>st</sup> glucose addition, which could have been a result of decreasing ambient  $\text{NO}_3^-$  concentrations as observed in monthly autumn 2005 data. Furthermore,  $\text{NO}_3^-$  production from A1 and A12 during the 2<sup>nd</sup> glucose additions could have been the result of increasing ambient  $\text{NO}_3^-$  concentrations as seen in monthly autumn 2005 data. Ambient  $\text{NO}_3^-$  in A12 slightly increased prior to the  $\text{Br}^-$  and  $\text{NO}_3^-$  addition ( $0.15 \text{ mg N L}^{-1}$ ), which could explain the  $\text{NO}_3^-$  production during the  $\text{Br}^-$  and  $\text{NO}_3^-$  addition. Ambient  $\text{NO}_3^-$  concentrations measured before each addition for A3 remained relatively constant, which could partly explain the similar  $\text{NO}_3^-$  trends over time for each addition. Also, A12 ambient DOC concentrations remained similar throughout autumn 2005, thus explaining the little variation in DOC loss between the 1<sup>st</sup> glucose addition and the 2<sup>nd</sup> glucose addition. The average ambient  $\text{NO}_3^-$  and DOC concentrations used to calculate  $\text{NO}_3^-$  and DOC loss and production could be under- or overestimated. For example, ambient A1 and A11 DOC concentrations during autumn 2005 increased from September to October. Because the 1<sup>st</sup> glucose additions began in September, incoming ambient DOC concentrations for A1 and A11 could be increasing throughout the pull phase. The average ambient DOC concentrations could be lower on day 1 compared to the end of the pull phase. Therefore, increasing DOC concentrations over time or DOC production would occur in A1 and A11 for the 1<sup>st</sup> glucose addition.

Nitrification would also have resulted in  $\text{NO}_3^-$  production. Davidsson and Stahl (2000) determined that nitrification was positively correlated to pH.

Because pH generally increased immediately after the push phase for each addition for each well, nitrification might have been stimulated and resulted in  $\text{NO}_3^-$  production. However,  $\text{NO}_3^-$  production was not strongly correlated to pH for each well for each addition. Furthermore,  $\text{NH}_4^+$  concentrations and  $\text{NO}_3^-$  loss and production trends were not negatively correlated.

Apparent production of  $\text{NO}_3^-$  and DOC could be attributed to  $\text{Br}^-$  adsorption to soil particles. Some anion adsorption capacity is found in temperate soils in the lower soil profile containing iron and aluminum oxides and hydroxides (Johnson et al., 1981; Johnson et al., 1986). The  $\text{Br}^-$  recovery rate would be faster if  $\text{Br}^-$  was adsorbing to soil particles. If only dilution was occurring within the wells, then the rate at which  $\text{Br}^-$  decreases would be faster than  $\text{NO}_3^-$  or DOC dilution. If  $\text{Br}^-$  was adsorbing to soil particles, but  $\text{NO}_3^-$  and DOC were not, there would have been an increase in  $\text{NO}_3^-$  and DOC concentrations relative to the  $\text{Br}^-$  recovery rate. Bromide adsorption might have caused apparent  $\text{NO}_3^-$  production within wells where  $\text{Br}^-$  breakthrough curves differed from each addition (A11 and A12). According to Groffman et al., (1995),  $\text{Br}^-$  inhibits microbial activity by decreasing rates of nitrification and mineralization, but not denitrification. Further research is needed to determine if  $\text{Br}^-$  adsorption does occur and what control mechanisms influence  $\text{Br}^-$  adsorption.

#### **Minimal $\text{NO}_3^-$ Loss**

Groundwater residence times could be too short for microbial activity to substantially influence  $\text{NO}_3^-$  and DOC concentrations. Altman and Parizek (1995) determined that groundwater dilution was a major contributor to  $\text{NO}_3^-$  loss

in a valley riparian setting. Even though slug tests estimated that A11 had the highest hydraulic conductivity, it was surprising that the  $\text{Br}^-$  recovery rate was the slowest compared to the rest of the addition wells. Longer groundwater residence times in soil with higher redox potential can result in significantly altered groundwater chemistry. Because A11 had longer groundwater residence times as well as high redox potential, this could explain why A11 had the highest variability with most chemical constituents.

Previous studies determined that hydraulic conductivities ranging from  $10^{-1}$  to  $10^{-2}$  are too fast for denitrification to take place (Burt et al., 1999; Puckett et al., 2002). The groundwater flows through the soil too quickly for microbial activities to reduce  $\text{NO}_3^-$  concentrations, resulting in minimal  $\text{NO}_3^-$  loss. Denitrification has been known to occur in soils with hydraulic conductivities ranging from  $10^{-3}$  to  $10^{-6}$  as seen in the James Farm wells. If relatively steep hill slopes were located next to the riparian zone, the hydraulic conductivities were higher relative to other parts of the riparian zone. The hillslope-derived  $\text{NO}_3^-$  inputs as well as  $\text{NO}_3^-$  retention would increase within a few meters in the riparian zone (Haycock and Pinay, 1993; Devito et al., 2000; Vidon and Hill, 2004a; Vidon and Hill, 2004b). Denitrification potential was higher further away from the stream next to steep hill slopes. There was a small hill west of the riparian zone close to A7 and A13 and a lawn located approximately 20 m from the hill slope. Perhaps the hydraulic conductivities were faster within the slope, thus carrying elevated  $\text{NO}_3^-$  concentrations (from lawn fertilizers or septage) into the riparian zone. This could explain the higher  $\text{NO}_3^-$  concentrations observed in A7. Studies estimating

denitrification potential in soils with hydraulic conductivities ranging from  $10^{-7}$  to  $10^{-9}$  have determined that riparian zone hydrogeomorphic characteristics explain why little to no  $\text{NO}_3^-$  loss occurred (Puckett and Hughes, 2005; Bohlke et al., 2007).

Oxic soil conditions inhibit denitrification. The heterogeneity of soils in the James Farm well field cause different rates at which oxygen diffused through the soil and into the groundwater. For example, soils with large pore sizes help increase air exchange, enhancing oxygen diffusion into the groundwater and resulting in oxic conditions (Burt et al. 2002). One reason why little, if any, denitrification occurred at James Farm was due to oxic groundwater. Hill et al. (2000) suggested that  $\text{NO}_3^-$  concentrations following a horizontal flow path decreased when DO concentrations were below  $3 \text{ mg L}^{-1}$ . Cey et al. (1999) found that  $\text{NO}_3^-$  concentrations decreased substantially when DO concentrations were below  $2 \text{ mg L}^{-1}$ . Low DO concentrations were associated with the  $\text{NO}_3^-$  loss that occurred during the  $\text{Br}^-$  and  $\text{NO}_3^-$  addition and 1<sup>st</sup> glucose addition in A11. However,  $\text{NO}_3^-$  production occurred from day 2 through the rest of the pull phase even though DO concentrations were below  $3 \text{ mg L}^{-1}$ . Dissolved oxygen concentrations in A12 were less than  $4 \text{ mg L}^{-1}$  for some sampling days during the 1<sup>st</sup> glucose addition, which could have been low enough to influence the observed  $\text{NO}_3^-$  loss from day 1 through day 4. A1 also had DO concentrations below  $4 \text{ mg L}^{-1}$  for some sampling days during the  $\text{Br}^-$  and  $\text{NO}_3^-$  addition, which could partly explain the observed  $\text{NO}_3^-$  loss.

Temperature did not seem to directly influence  $\text{NO}_3^-$ , but may have



influenced DOC. Even though temperatures were similar during the  $\text{Br}^-$  and  $\text{NO}_3^-$  addition and the 1<sup>st</sup> glucose addition,  $\text{NO}_3^-$  loss and production trends between each well were not similar. Dissolved organic carbon losses were greater during the 2<sup>nd</sup> glucose addition when temperatures were substantially lower.

Because the water table was near the soil surface and aquicludes were below the screened portion of the well, infiltrating precipitation could have diluted groundwater somewhat quickly. Large rain events might not have substantially influenced A12 compared to the other wells because relatively deep groundwater could be infiltrating A12 due to relatively high monthly  $\text{SiO}_2$  concentrations. Bedrock weathering is a source of  $\text{SiO}_2$ . Deeper groundwater would accumulate  $\text{SiO}_2$  and have higher  $\text{SiO}_2$  concentrations than shallow groundwater. Precipitation does not contain  $\text{SiO}_2$ , therefore when large rain events occur infiltrating precipitation dilutes groundwater  $\text{SiO}_2$  concentrations. Because A11 had the lowest monthly mean  $\text{SiO}_2$  concentrations, perhaps the groundwater source is shallow and large rain events could have influenced  $\text{SiO}_2$  concentrations.

Precipitation events seemed to have influenced  $\text{NO}_3^-$  and DOC trends over time. Precipitation  $\text{NO}_3^-$  concentrations could have influenced groundwater  $\text{NO}_3^-$  loss and production trends for A11. Precipitation infiltrating the surrounding soil of A11 could take longer to enter A11 groundwater because  $\text{NO}_3^-$  loss decreased and DOC production increased 2 to 3 days after precipitation events occurred during the 1<sup>st</sup> glucose additions and 2<sup>nd</sup> glucose additions. Precipitation

might not have influenced  $\text{NO}_3^-$  and DOC trends over time for A3 because  $\text{NO}_3^-$  and DOC loss and production was fairly consistent during each addition with the exception of slightly decreasing DOC loss during the 2<sup>nd</sup> glucose addition rain event.

Precipitation events could have increased groundwater DOC concentrations by raising the water table to the organic soil horizon and mobilize ambient DOC within the soil. An increase of DOC in groundwater could be attributed to rain passing through the forest canopy and collecting DOC from leaf washing and leaf leaching (Tukey, 1970; McDowell and Likens, 1988). Because the 1<sup>st</sup> glucose additions and 2<sup>nd</sup> glucose additions were conducted when large amounts of leaf litter was found on the forest floor, perhaps large rain events leaching nutrients from the leaf litter increased DOC concentrations over time.

Different groundwater sources could be altering groundwater chemistry in the James Farm wells field. Even though precipitation events could have influenced groundwater  $\text{NO}_3^-$  and DOC concentrations, the wells did not demonstrate similar  $\text{NO}_3^-$  and DOC influences over time. Variable anion and cation concentrations between months with no seasonal trends could be attributed to different groundwater sources over time. The large increase in groundwater elevation and decrease in overall  $\text{SiO}_2$  concentrations further demonstrates variable groundwater sources. Ambient chemical constituents demonstrated daily variations throughout the 3 days prior to each addition push phase. The groundwater source in any one well is not consistent over time.

Groundwater table elevations could have directly influenced  $\text{NO}_3^-$

concentrations. Alternating water table fluctuations creating aerobic and anaerobic conditions in the soil enhance organic matter mineralization and  $\text{NO}_3^-$  loss by denitrification (Reddy and Patrick 1975). Hefting et al. (2004) determined that the water table elevation was the main determinant of groundwater N dynamics. Denitrification was the major contributor to N loss when the range of distance from the soil surface to the groundwater table was 10 to 30 cm. Autumn 2005 water table elevations in A1, A11, A12, and A3 did range from about 10 to 30 cm below the soil surface. A3  $\text{NO}_3^-$  concentrations remained similar throughout autumn 2005. A12 and A1  $\text{NO}_3^-$  concentrations increased from September to October while the groundwater tables were 24 cm and 13 cm below the soil surface, respectively. Monthly groundwater table elevations did not seem to directly influence N species concentrations.

Hill et al. (2000) determined that denitrification “hotspots” were located near soil interfaces between sands and either peats or buried river channel deposits. However, the hotspots became N-limited in the narrow zone of  $\text{NO}_3^-$  consumption. Because  $1.5 \text{ mg N L}^{-1}$  of  $\text{NO}_3^-$  was added during the push phase of the  $\text{Br}^-$  and  $\text{NO}_3^-$  additions and the 1<sup>st</sup> glucose additions, perhaps the added  $\text{NO}_3^-$  was not enough to eliminate the N limitation possibly occurring in the James Farm well field. Even though  $4.5 \text{ mg N L}^{-1}$  of  $\text{NO}_3^-$  was added during the 2<sup>nd</sup> glucose addition,  $87.17 \text{ mg C L}^{-1}$  added was perhaps enough to result in N limitation once again.

### **$\text{SO}_4^{2-}$ Trends**

In general,  $\text{SO}_4^{2-}$  concentrations decreased with each consecutive addition

for all wells, however  $\text{SO}_4^{2-}$  concentrations increased from ambient concentrations during the additions. Decreasing  $\text{SO}_4^{2-}$  concentrations with each consecutive addition could be attributed to decreasing incoming ambient  $\text{SO}_4^{2-}$  concentrations. For example, autumn 2005 ambient  $\text{SO}_4^{2-}$  concentrations decreased in A11 and A12. However, autumn 2005 ambient  $\text{SO}_4^{2-}$  concentrations in A3 remained similar and increased in A1. Therefore, decreasing ambient  $\text{SO}_4^{2-}$  concentrations do not fully explain  $\text{SO}_4^{2-}$  decreasing for all wells. Turner et al (1980) determined plants may accumulate  $\text{SO}_4^{2-}$  in their leaf tissue if there is a large amount of  $\text{SO}_4^{2-}$  in the soil. Even though the vegetation in James Farm could have decreased ambient groundwater  $\text{SO}_4^{2-}$  concentrations due to  $\text{SO}_4^{2-}$  accumulation within their leaf tissues, the additions occurred during leaf senescence, which would have resulted in less plant  $\text{SO}_4^{2-}$  uptake. Decreasing  $\text{SO}_4^{2-}$  concentrations due to reduction of  $\text{SO}_4^{2-}$  or plant uptake can be linked to consumption of  $\text{H}^+$  ions and increase soil pH (Binkley and Richter, 1987). Although pH increased immediately after the push phase of almost every addition for all wells, the only time pH increased while  $\text{SO}_4^{2-}$  decreased was with A1 during the 1<sup>st</sup> glucose addition.

One explanation for  $\text{SO}_4^{2-}$  increasing from ambient concentrations could be attributed to flushing  $\text{SO}_4^{2-}$  out of the surrounding soil due to pushing 10 L of the groundwater solution into the well. The  $\text{SO}_4^{2-}$  leached out of the surrounding soil could have adsorbed in lower soil profiles. The highest rates of  $\text{SO}_4^{2-}$  adsorption occur most often in the B horizon and microbial immobilization of added  $^{35}\text{SO}_4^{2-}$  occurs within the upper soil horizon (Schindler et al., 1986;

Randlett et al., 1992). Perhaps as more groundwater was flushed through the soil with each consecutive addition,  $\text{SO}_4^{2-}$  adsorbed to soil layers in the B horizon.

### **Cation Exchange Capacity**

As cations move through the soil,  $\text{SO}_4^{2-}$  acts as a balancing anion. Because  $\text{SO}_4^{2-}$  concentrations decreased with each consecutive addition, perhaps  $\text{SO}_4^{2-}$  acted as the balancing anion for  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ . However, there were not any positive or negative correlations over time for each addition for each well when observing  $\text{SO}_4^{2-}$  and cation concentrations. Sulfate might have acted as a balancing anion for  $\text{Na}^+$  in A11 during the 2<sup>nd</sup> glucose addition due to a large decrease in  $\text{SO}_4^{2-}$  and  $\text{Na}^+$  concentrations on day 5. The large decrease in  $\text{SO}_4^{2-}$  could also suggest  $\text{SO}_4^{2-}$  reduction. However, a large decrease in  $\text{Na}^+$  occurring the same day suggests groundwater sources were changing over time.

Cation exchange capacity could be altered by the relatively large amounts of added DOC into the well field. Dissolved organic carbon affects soil structure by coating clay particles with organic matter. Dissolved organic carbon sorption increases in mineral soil depth and abiotic DOC adsorption occurs with reactive sesquioxides in the soil (McDowell and Wood, 1984; Moore et al., 1992). Because a substantial amount of DOC is added during 2<sup>nd</sup> glucose additions compared to the other additions, the DOC could have covered large amounts of surrounding soil particles. Sodium loss was the highest during these additions even though the 2<sup>nd</sup> glucose additions pushed the most  $\text{Na}^+$  into the wells.

Perhaps  $\text{Na}^+$  adsorbed to the DOC covering the clay particles, thus substantially reducing  $\text{Na}^+$  concentrations within the groundwater. Because  $\text{Ca}^{2+}$  concentrations were generally lowest during the 2<sup>nd</sup> glucose additions perhaps the increased DOC concentrations also influenced  $\text{Ca}^{2+}$  concentrations. Further research is needed to determine if CEC is affected by the push-pull method and whether increased inputs of  $\text{Na}^+$ ,  $\text{NO}_3^-$ , and DOC affect CEC.

### **Where is the N Going?**

The Lamprey River watershed currently retains approximately 90% of the N that enters the basin (Daley, pers. comm). The James Farm riparian soil composition and vertical heterogeneity are similar to most riparian zones located throughout the Lamprey River watershed. The push-pull method did not demonstrate N removal within the James Farm riparian zone. However, wetlands in the Lamprey River watershed have demonstrated  $\text{NO}_3^-$  loss. Flint (2007) measured surface- and groundwater  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , DOC, and dissolved organic nitrogen (DON) concentrations directly up- and downstream from 11 wetlands in the Lamprey River watershed. Her study determined that  $\text{NO}_3^-$  concentrations significantly decreased while DON and DOC concentrations significantly increased between up- and downstream sampling stations.

Perhaps DON is increasing downstream due to DON accumulation in surface- and groundwater from leaf leachate or leaf litter decomposition in the Lamprey River watershed wetlands. However, DON concentrations during months with large precipitation events were not significantly different from any other months (Flint, 2007). Furthermore, DON concentrations were low

throughout the James Farm riparian zone even during autumn leaf senescence. Because of low riparian DON concentrations and minimal  $\text{NO}_3^-$  loss as well as increased DON output correlated to wetland  $\text{NO}_3^-$  loss, perhaps DON concentrations and  $\text{NO}_3^-$  removal are interconnected. Dail et al. (2001) determined that large additions of  $^{15}\text{N}-\text{NO}_3^-$  to soils quickly disappeared and were recovered in the soil as DON. Watanabe (2006) determined that DON retention increased in temperate soils upon  $\text{NO}_3^-$  addition. Future studies should assess DON concentrations when estimating  $\text{NO}_3^-$  loss in either riparian zones or wetlands.

Soil organic matter (SOM) could also influence N loss. Humus is formed by continual modification of initial labile carbon molecules. One hypothesis for humus reactions with other compounds is larger and larger molecules of organic matter are formed with increased amounts of nitrogen added to the molecules as proteins (Schnitzer, 1978; Mellilo et al., 1989). Humus concentrations increase with soil depth and the dissolved organic matter can adsorb to mineral soils (McDowell and Wood, 1984). The Lamprey River watershed N retention could be from accumulation of N attached to SOM adsorbed to mineral soils. In suburban and urban areas, clearing of vegetation for residential and commercial developments decreases overall inputs of C, however increased N inputs continue with increasing human population density. As labile C decomposition results in more humus, there is an increase in SOM. When comparing urban and rural forests with the same species and soil types, urban forests have 30% higher soil organic matter (Groffman et al, 1995). The amount of soil organic matter

could be increasing in suburban areas as well as contributing to N removal from N attached to accumulating SOM as proteins.

Hydrogeologic characteristics also influence N species composition and concentrations. Redoximorphic soil conditions in riparian zones are favorable for N loss. Groundwater flow will follow the path of least resistance. Perhaps higher rates of denitrification occur in the clay layers while added  $\text{NO}_3^-$  from upslope anthropogenic activities flows more quickly through soil layers with higher hydraulic conductivities and with little microbial influence on N concentrations. Groundwater with relatively high amounts of  $\text{NO}_3^-$  could follow vertical flow paths with high hydraulic conductivity resulting in increased concentrations with soil depth eventually accumulating in bedrock fractures.

Because the James Farm riparian zone hydrogeologic characteristics are similar to other riparian zones throughout the Lamprey River watershed, riparian zones in this basin might not be effective at N removal compared to wetlands. Observing differences of  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , TDN, and DOC concentrations between wetlands and riparian zones could determine which landscape feature is more efficient at N removal. If there is a difference in N loss, wetlands and riparian zones should both be considered when developing N budgets in watershed models to help resolve the history and fate of N at the regional and global scale.



## CHAPTER IV

### CONCLUSION

Nitrogen dynamics in riparian zones are complex. When assessing riparian zone denitrification potential, it is important to consider hydrogeomorphic characteristics such as physical soil properties, soil chemical composition and moisture, nutrient availability, groundwater dynamics, and microbial community structure. Because human population density is significantly correlated to  $\text{NO}_3^-$  concentrations in surface- and groundwater and global human population continues to grow exponentially,  $\text{NO}_3^-$  concentrations entering surface- and groundwater will increase over time (Smil, 1997; Vitousek et al., 1997b; Daley, 2002). Previous experiments have determined that some riparian zones exhibit high rates of denitrification and some do not. Understanding control mechanisms of denitrification is essential to accurately estimating N storage and loss terms, maximizing the effectiveness of remediation efforts, and protecting and sustaining drinking water sources for future generations.

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**Table 1.** James Farm soil profiles from wells A1, A3, A6, and A7. Soil profiles for A6 and A7 were used to estimate soil profiles for A11 and A12, respectively.

<b>A1</b>		<b>A3</b>	
<b>Depth (cm)</b>	<b>Description</b>	<b>Depth (cm)</b>	<b>Description</b>
0-10	OM	0-10	OM
10-36	loamy clay	10-15	mineral
36-50	silty clay	15-20	clayey loam
50-60	loamy clayey sand	20-32	sandy clayey loam
60-70	mottled clay (massive structure)	32-47	clayey sand (oxidated)
70-95	clay (massive structure)	47-62	clayey sand (elluvial)
95-109	fine sandy clay	62-82	silty sandy clay
109-121	clay	82-92	clayey sand
121-142	clay	92-102	mottled clayey sand (much coarser)
		102-112	mottled clayey sand (coarser)
		112-122	clayey gravelly sand (coarser)
		122-142	silty clay
		142-158	mottled clay (massive structure)

<b>A11 (as A6)</b>		<b>A12 (as A7)</b>	
<b>Depth (cm)</b>	<b>Description</b>	<b>Depth (cm)</b>	<b>Description</b>
0-5	OM (anaerobic)	0-10	organic
5-26	mineral (anaerobic)	10-39	fine white sand w/ oxidation
26-40	clayey loam (anaerobic)	39-45	med coarse sand
40-45	reduced sand (anaerobic)	45-55	gravelly sand
45-55	sandy clay (blue)	55-68	mottled clay (massive structure)
55-63	mottled silty clay	68-80	mottled clay (massive structure)
63-64	sandy clay (blue)	80-90	mottled clay (massive structure)
64-76	sandy clay (small rocks)		

**Table 2.** Hydraulic conductivities for each well were determined by slug tests (June 2006). Hydraulic conductivities were calculated using data within approximately the third minute of the slug tests.

<b>Well</b>	<b>Hydraulic Conductivity (cm sec<sup>-1</sup>)</b>
<b>A1</b>	$6.01 \times 10^{-4}$
<b>A11</b>	$2.00 \times 10^{-3}$
<b>A12</b>	$9.33 \times 10^{-5}$
<b>A3</b>	$1.78 \times 10^{-3}$

**Table 3.** Concentrations ( $\text{mg L}^{-1}$ ) of added bromide ( $\text{Br}^-$ ), nitrate ( $\text{NO}_3^-$ ), and glucose (DOC) for each push-pull addition.

	<b><math>\text{Br}^-</math> &amp; <math>\text{NO}_3^-</math> Addition</b>	<b>1<sup>st</sup> Glucose Addition</b>	<b>2<sup>nd</sup> Glucose Addition</b>
<b><math>\text{Br}^-</math> (<math>\text{mg L}^{-1}</math>)</b>	7.1	7.1	20.0
<b><math>\text{NO}_3^-</math>-N (<math>\text{mg L}^{-1}</math>)</b>	1.5	1.5	4.5
<b>DOC (<math>\text{mg L}^{-1}</math>)</b>	0.0	2.4	87.2

**Table 4.** Mean concentrations and standard errors of James Farm groundwater physical properties, such as pH, specific conductivity (EC), temperature, and dissolved oxygen (DO) and groundwater chemical constituents, such as nitrate ( $\text{NO}_3^-$ ), ammonium ( $\text{NH}_4^+$ ), total dissolved nitrogen (TDN), and dissolved organic carbon (DOC).

Wells	pH	EC ( $\mu\text{S cm}^{-1}$ )	Temperature ( $^{\circ}\text{C}$ )	DO ( $\text{mg L}^{-1}$ )	$\text{NO}_3^-$ ( $\text{mg N L}^{-1}$ )	$\text{NH}_4^+$ ( $\mu\text{g N L}^{-1}$ )	TDN ( $\text{mg N L}^{-1}$ )	DOC ( $\text{mg C L}^{-1}$ )
A1	$6.86 \pm 0.07$	$372 \pm 15$	$9.83 \pm 0.9$	$6.59 \pm 0.48$	$1.84 \pm 0.11$	$13 \pm 2$	$1.85 \pm 0.11$	$0.94 \pm 0.08$
A2	$7.21 \pm 0.08$	$455 \pm 16$	$9.36 \pm 0.87$	$9.49 \pm 0.5$	$2.3 \pm 0.11$	$11 \pm 2$	$2.51 \pm 0.09$	$0.86 \pm 0.08$
A3	$7.28 \pm 0.07$	$446 \pm 16$	$9.54 \pm 0.71$	$6.91 \pm 0.33$	$1.73 \pm 0.07$	$7 \pm 1$	$1.85 \pm 0.05$	$0.59 \pm 0.05$
A4	$7.19 \pm 0.06$	$354 \pm 34$	$10.14 \pm 1$	$6.23 \pm 0.46$	$0.74 \pm 0.07$	$12 \pm 2$	$0.99 \pm 0.08$	$1 \pm 0.11$
A5	$7.1 \pm 0.08$	$470 \pm 18$	$10.05 \pm 1.1$	$4.71 \pm 0.73$	$1.11 \pm 0.13$	$236 \pm 65$	$1.44 \pm 0.13$	$2.14 \pm 0.68$
A7	$6.89 \pm 0.06$	$389 \pm 14$	$9.93 \pm 1.08$	$7.61 \pm 0.44$	$1.63 \pm 0.14$	$15 \pm 2$	$2.02 \pm 0.08$	$0.84 \pm 0.1$
A8	$6.75 \pm 0.08$	$300 \pm 22$	$10.3 \pm 1.17$	$5.91 \pm 0.45$	$0.69 \pm 0.1$	$16 \pm 3$	$0.87 \pm 0.14$	$2.33 \pm 0.22$
A9	$7.25 \pm 0.11$	$464 \pm 16$	$10.26 \pm 1.34$	$9.15 \pm 0.42$	$2 \pm 0.04$	$31 \pm 5$	$2.21 \pm 0.06$	$1.53 \pm 0.13$
A10	$7.19 \pm 0.26$	$399 \pm 9$	$10.11 \pm 1$	$6.92 \pm 0.48$	$1.13 \pm 0.15$	$26 \pm 6$	$1.27 \pm 0.08$	$1.13 \pm 0.15$
A11	$6.83 \pm 0.09$	$320 \pm 18$	$9.91 \pm 1.27$	$7.07 \pm 0.49$	$0.57 \pm 0.07$	$15 \pm 2$	$0.74 \pm 0$	$2.61 \pm 0.27$
A12	$6.18 \pm 0.3$	$405 \pm 27$	$9.63 \pm 1$	$6.69 \pm 0.5$	$2.19 \pm 0.05$	$20 \pm 4$	$2.22 \pm 0.05$	$0.69 \pm 0.07$
A13	$6.8 \pm 0.06$	$355 \pm 12$	$9.49 \pm 0.93$	$7.77 \pm 0.38$	$1.79 \pm 0.07$	$18 \pm 3$	$1.91 \pm 0.08$	$1.01 \pm 0.15$
JF-Staff	$7.19 \pm 0.08$	$256 \pm 13$	$10.25 \pm 1.34$	$11.23 \pm 0.78$	$0.8 \pm 0.05$	$12 \pm 2$	$0.93 \pm 0.05$	$2.62 \pm 0.25$

**Table 5.** There were significant differences of mean nitrate ( $\text{NO}_3^-$ ) between the James Farm groundwater wells. Wells with different letters represent wells with significantly different mean groundwater  $\text{NO}_3^-$ .

Well		Mean
A2	A	2.41
A12	A B	2.21
A9	A B	2.00
A7	B	1.90
A1	B	1.83
A13	B	1.79
A3	B	1.76
A10	C	1.07
A5	C	1.04
A4	C	0.90
JF-Staff	C	0.80
A8	C	0.73
A11	C	0.61

**Table 6.** There were significant differences of mean dissolved organic carbon (DOC) between the James Farm groundwater wells. Wells with different letters represent wells with significantly different mean groundwater DOC.

Well		Mean
JF-Staff	A	2.62
A11	A	2.61
A8	A	2.33
A9	B	1.53
A5	B C	1.25
A10	B C	1.13
A13	B C	1.01
A4	B C	1.00
A1	B C	0.94
A2	B C	0.86
A7	B C	0.84
A12	C	0.64
A3	C	0.59

**Table 7.** Mean concentrations and standard errors of sodium ( $\text{Na}^+$ ), magnesium ( $\text{Mg}^{2+}$ ), calcium ( $\text{Ca}^{2+}$ ), potassium ( $\text{K}^+$ ), bromide ( $\text{Br}^-$ ), sulfate ( $\text{SO}_4^{2-}$ ), and silica ( $\text{SiO}_2$ ) in the James Farm groundwater.

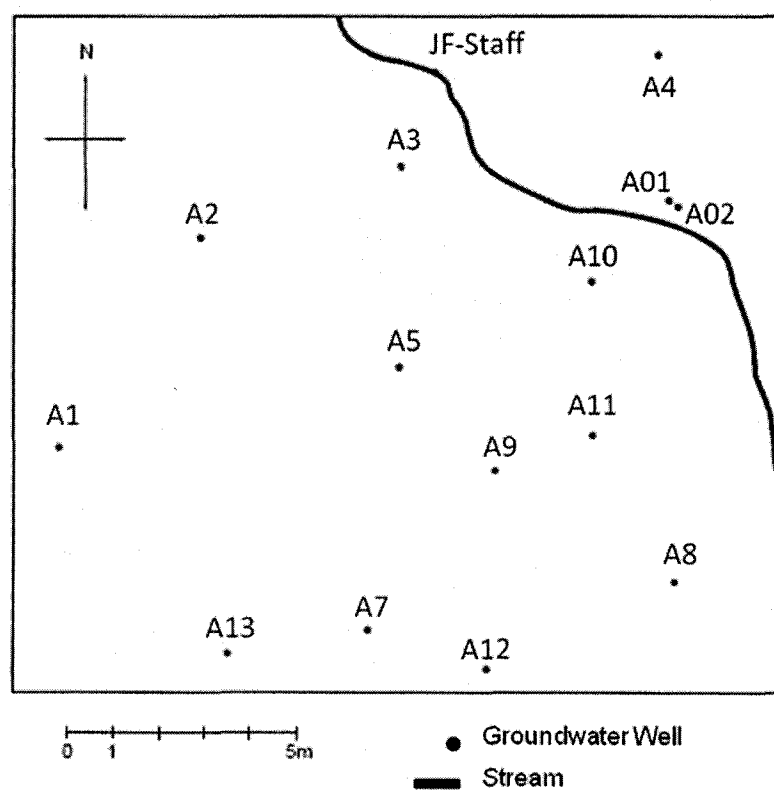
Wells	$\text{Na}^+$ (mg L <sup>-1</sup> )	$\text{Mg}^{2+}$ (mg L <sup>-1</sup> )	$\text{Ca}^{2+}$ (mg L <sup>-1</sup> )	$\text{K}^+$ (mg L <sup>-1</sup> )	$\text{Br}^-$ (mg L <sup>-1</sup> )	$\text{Cl}^-$ (mg L <sup>-1</sup> )	$\text{SO}_4^{2-}$ (mg S L <sup>-1</sup> )	$\text{SiO}_2$ (mg L <sup>-1</sup> )
<b>A1</b>	14.96 ± 0.33	9.27 ± 0.24	28.62 ± 2.4	1.26 ± 0.04	0.04 ± 0.01	56.44 ± 2.36	3.44 ± 0.08	16.03 ± 1.16
<b>A2</b>	15.77 ± 0.54	13.29 ± 0.37	28.44 ± 2.55	1.52 ± 0.06	0.09 ± 0.02	63.12 ± 2.92	3.67 ± 0.1	13.75 ± 1.14
<b>A3</b>	16 ± 0.19	13.25 ± 0.06	27.39 ± 2.61	1.32 ± 0.03	0.05 ± 0.01	61.82 ± 2.33	3.85 ± 0.05	13.67 ± 1.27
<b>A4</b>	15.63 ± 0.33	12.44 ± 0.25	27.51 ± 2.73	1.44 ± 0.07	0.03 ± 0.01	60.25 ± 2.3	4.67 ± 0.09	12.86 ± 1.33
<b>A5</b>	16.46 ± 0.72	13.43 ± 0.57	30.53 ± 3.34	1.64 ± 0.15	0.09 ± 0.02	60.71 ± 2.72	2.74 ± 0.22	15.63 ± 1.24
<b>A7</b>	14.79 ± 0.43	9.48 ± 0.13	29.92 ± 2.74	1.22 ± 0.04	0.07 ± 0.02	57.73 ± 2.22	3.39 ± 0.06	18.82 ± 1.71
<b>A8</b>	10.4 ± 0.92	9.66 ± 0.71	25.44 ± 2.6	1.27 ± 0.15	0.02 ± 0.01	37.51 ± 4.3	3.08 ± 0.24	11.43 ± 1.03
<b>A9</b>	15.87 ± 0.29	13.65 ± 0.24	26.39 ± 3	2.96 ± 1.38	0.11 ± 0.03	61.43 ± 3	3.52 ± 0.06	17.37 ± 1.27
<b>A10</b>	14.15 ± 0.31	12.95 ± 0.25	26.71 ± 2.83	1.53 ± 0.12	0.05 ± 0.05	58.31 ± 2.4	4.06 ± 0.09	14.45 ± 0.99
<b>A11</b>	11.49 ± 0.6	10.59 ± 0.44	26.5 ± 2.31	0.92 ± 0.06	0.06 ± 0.02	42.98 ± 7.82	3.42 ± 0.19	12.42 ± 1.25
<b>A12</b>	15.36 ± 0.23	10.05 ± 0.04	31.13 ± 2.56	1.46 ± 0.15	0.03 ± 0.01	61.44 ± 2.25	3.5 ± 0.05	17.3 ± 1.58
<b>A13</b>	13.06 ± 0.25	9.5 ± 0.18	25.71 ± 2.1	1.5 ± 0.06	0.12 ± 0.05	51.35 ± 1.64	3.26 ± 0.06	15.72 ± 1.3
<b>JF-Staff</b>	23.71 ± 1	4.87 ± 0.21	13.94 ± 0.7	1.22 ± 0.05	0.01 ± 0	48.37 ± 3.19	3.55 ± 0.1	8.35 ± 0.5

**Table 8.** Nitrate ( $\text{NO}_3^-$ ), ammonium ( $\text{NH}_4^+$ ), total dissolved nitrogen (TDN), and dissolved organic carbon (DOC) concentrations of precipitation from rain events that occurred throughout the push-pull additions.

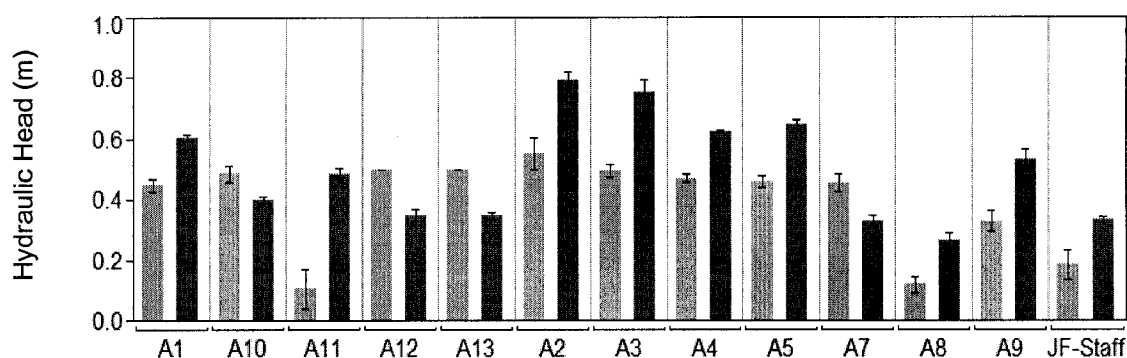
UNH #	Date	$\text{NO}_3^-$ (mg N L <sup>-1</sup> )	DOC (mg C L <sup>-1</sup> )	$\text{NH}_4^+$ ( $\mu\text{g N L}^{-1}$ )	TDN (mg N L <sup>-1</sup> )
62613	09/05/06	0.05	0.46	33	0.11
62740	09/06/06	0.20	2.98	212	0.55
63299	09/15/06	0.19	0.63	31	0.24
63422	09/21/06	0.27	1.65	313	0.61
63529	09/25/06	0.75	1.43	401	1.15
63557	09/29/06	0.15	.	.	.
63967	10/23/06	0.41	0.78	292	0.73
64181	10/30/06	0.04	0.20	30	0.08
64337	11/03/06	0.68	0.95	337	1.01
64338	10/30/06	0.05	0.15	32	0.10
64356	11/08/06	0.20	0.30	94	0.30
64357	11/09/06	0.02	0.06	15	0.05
64358	11/09/06	0.04	0.05	12	0.08



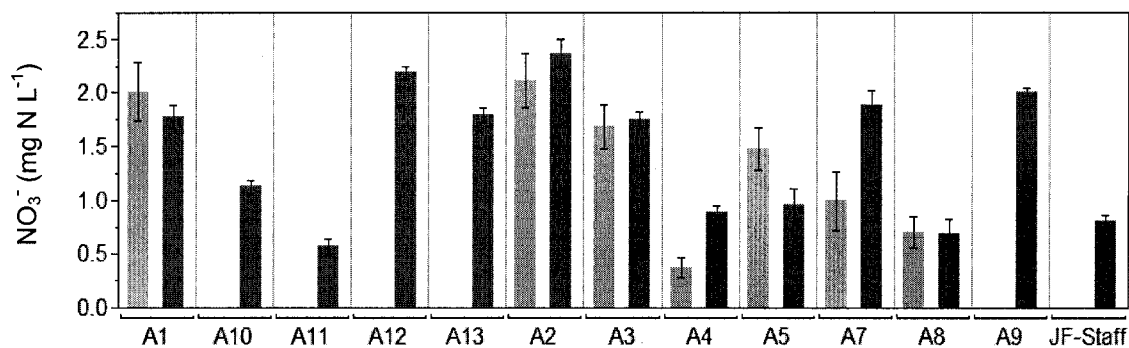
## James Farm Well Field



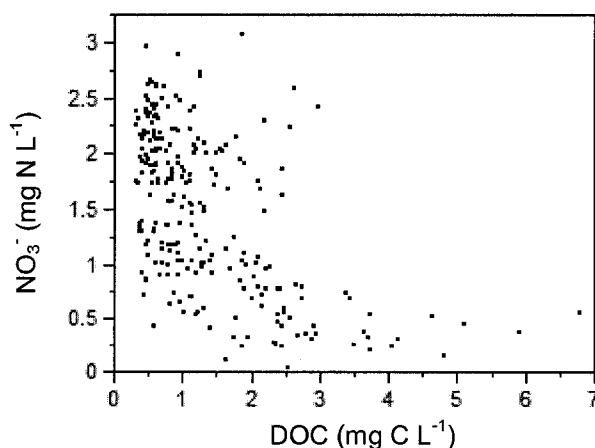
**Figure 1.** The James Farm riparian well field is located in the conservation area in the James Farm housing development in Lee, New Hampshire. There were 14 PVC groundwater wells with 5.08 cm diameters as well as a staff in the stream where stream water samples were taken. Groundwater flowed from the Northwest to the Southeast.



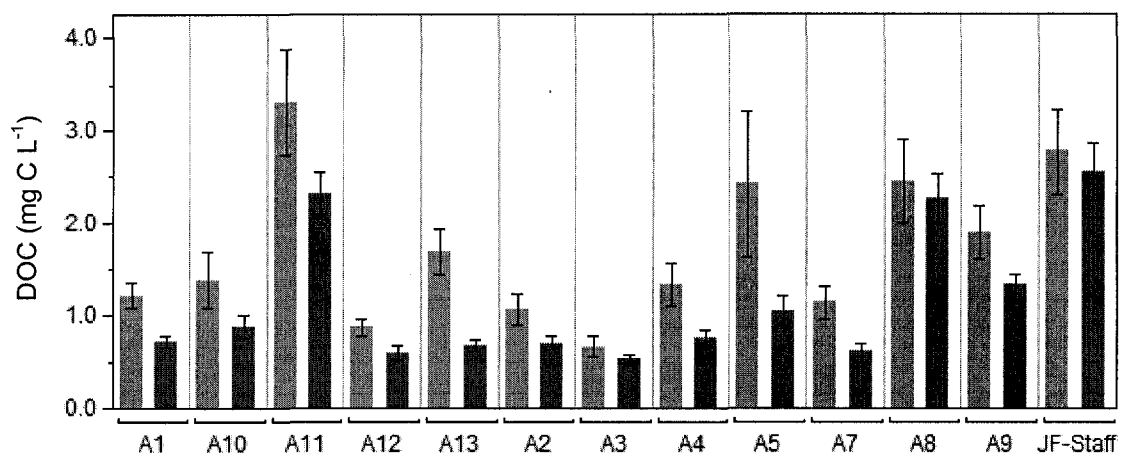
**Figure 2.** James Farm mean groundwater elevation, known as hydraulic head (m), and standard error determined by arbitrary datum. The light grey bars represent mean hydraulic head from July, 2004 to August, 2005 and the dark grey bars represent mean hydraulic head from September, 2005 to August, 2006. The James Farm well field was surveyed on July, 2004 and September, 2005.



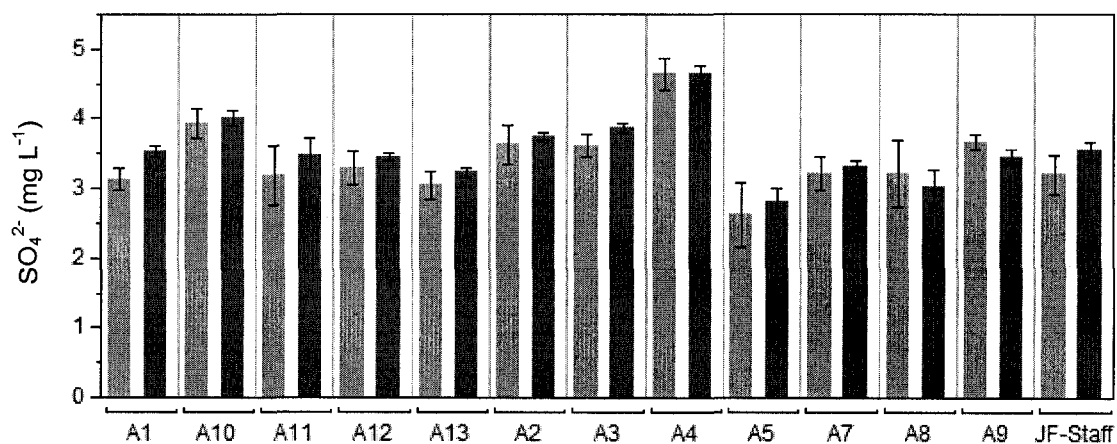
**Figure 3.** James Farm mean Nitrate ( $\text{NO}_3^-$ ) and standard error for each well during the sampling years. The light grey represents 1995-1996 and the medium grey represents 2004-2006.



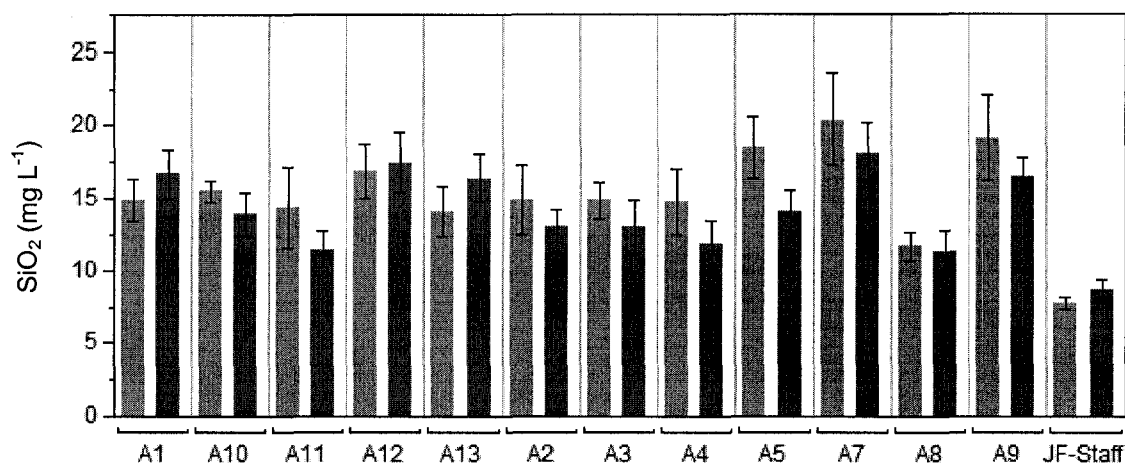
**Figure 4.** James Farm monthly groundwater nitrate ( $\text{NO}_3^-$ ) and dissolved organic carbon (DOC) concentrations ( $\text{mg L}^{-1}$ ) from all of the James Farm wells sampled from 27 July, 2004 through 13 August, 2006.



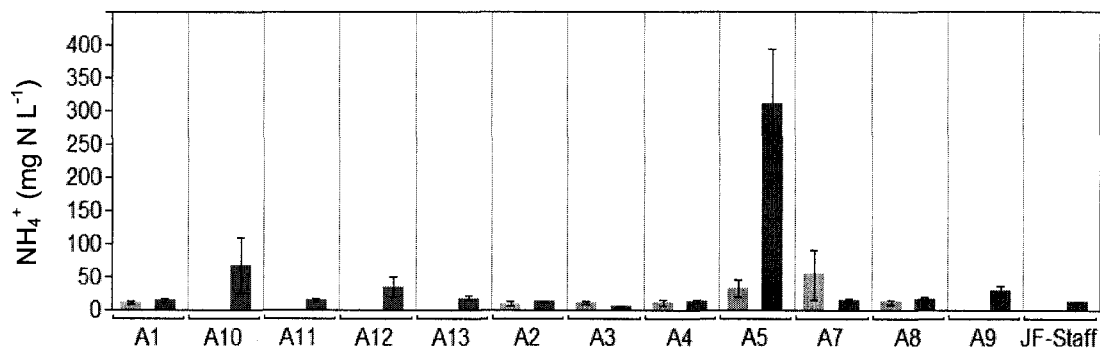
**Figure 5.** James Farm mean dissolved organic carbon (DOC) and standard error for each well during the sampling years. The light grey represents 2004-2005 and the dark grey represents 2005-2006.



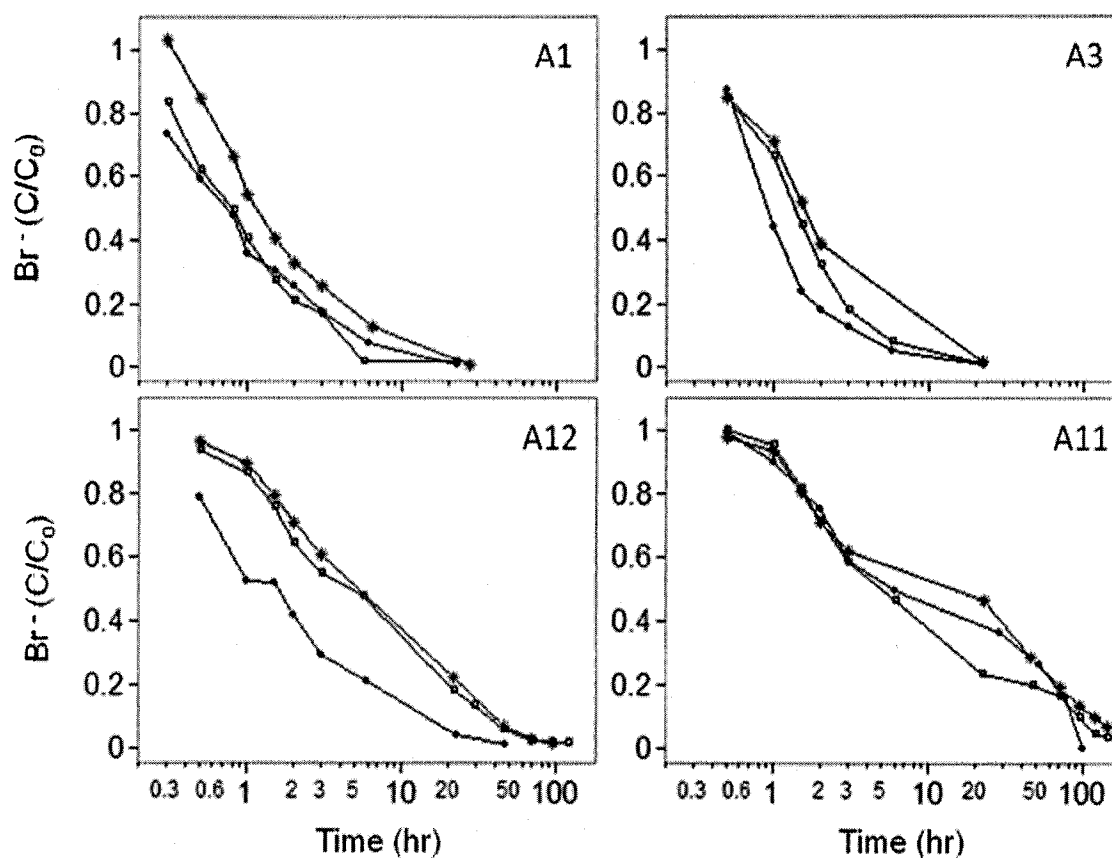
**Figure 6.** James Farm mean sulfate ( $\text{SO}_4^{2-}$ ) and standard error for each well during the sampling years. The light grey represents 2004-2005 and the dark grey represents 2005-2006.



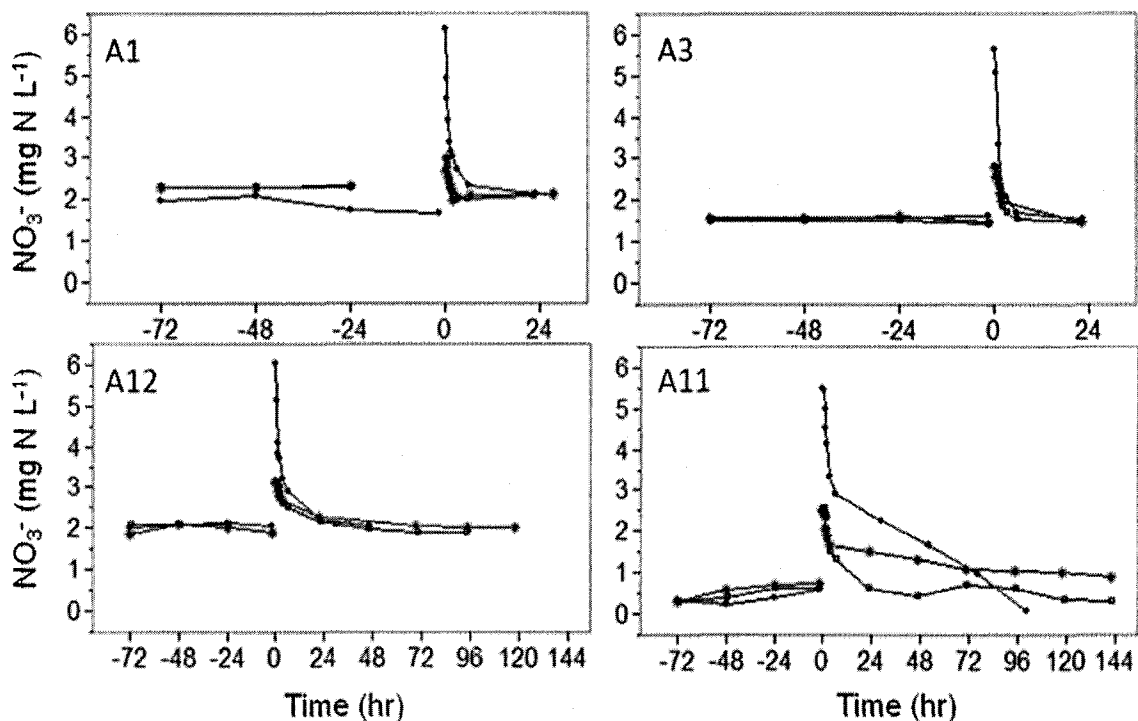
**Figure 7.** James Farm mean silica ( $\text{SiO}_2$ ) and standard error for each well during the sampling years. The light grey represents 2004-2005 and the dark grey represents 2005-2006.



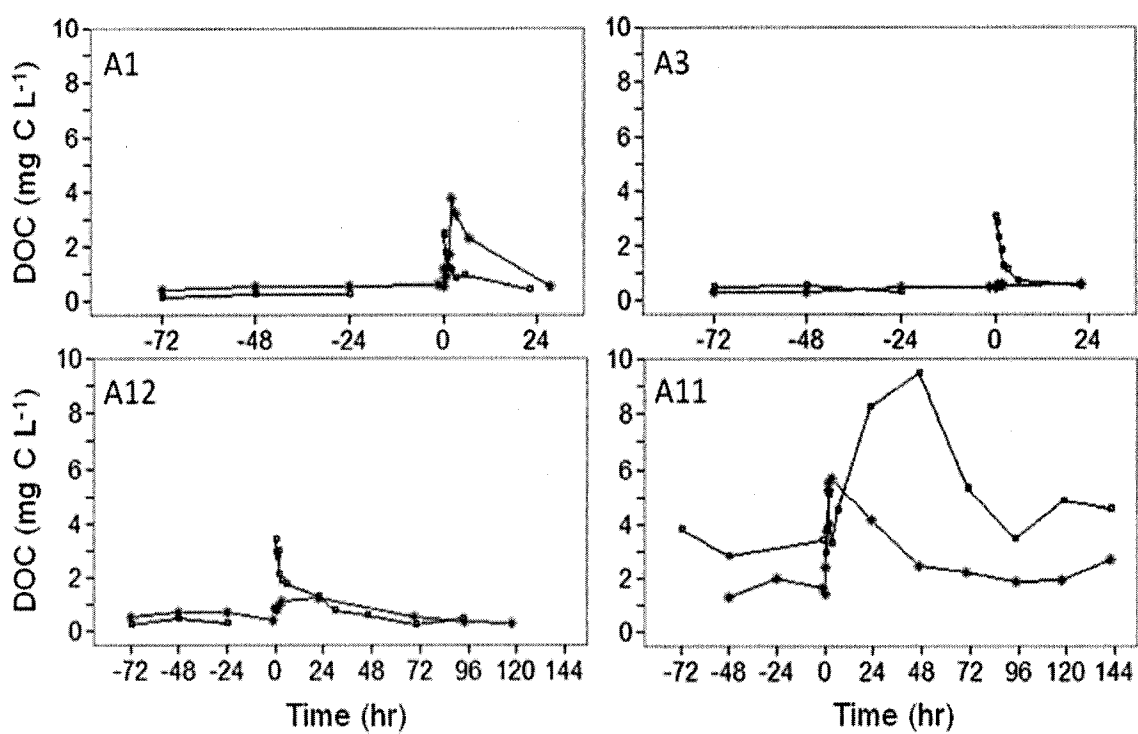
**Figure 8.** James Farm mean ammonium ( $\text{NH}_4^+$ ) and standard error for each well during the sampling years. The light grey represents 1995-1996 and the dark grey represents 2004-2006.



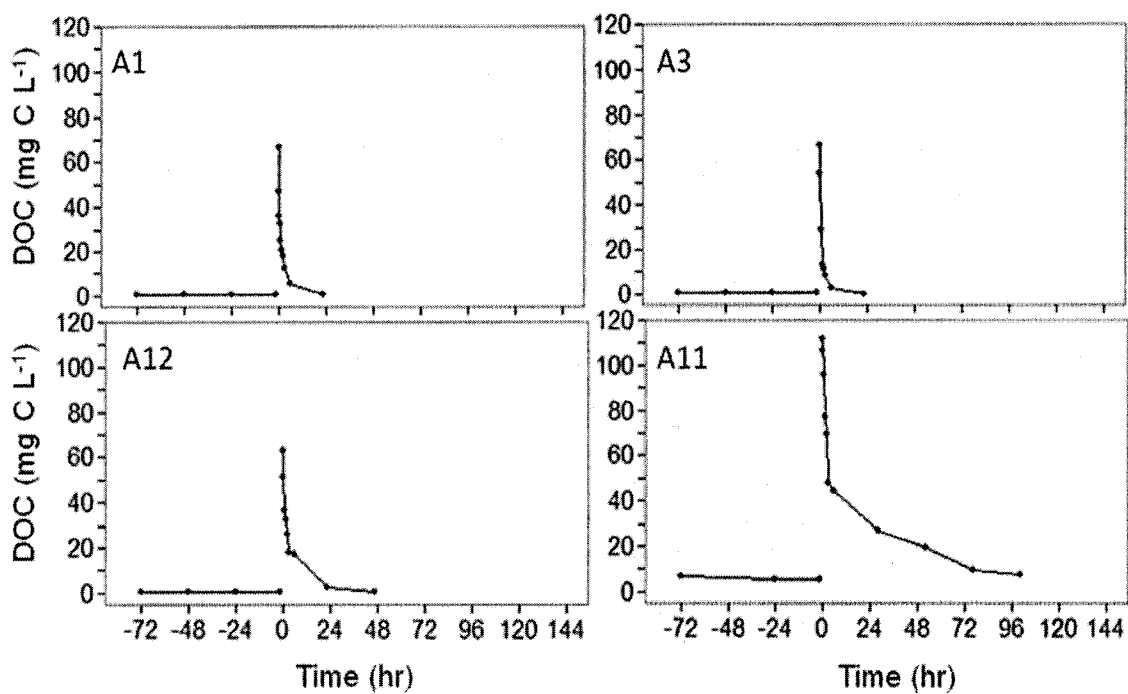
**Figure 9.** Bromide breakthrough curves, known as tracer recovery rates, for each addition. The symbol \* represents the  $Br^-$  and  $NO_3^-$  addition,  $\square$  represents the 1<sup>st</sup> glucose addition, and  $\bullet$  represents the 2<sup>nd</sup> glucose addition.



**Figure 10.** Nitrate ( $\text{NO}_3^-$ ) concentrations ( $\text{mg N L}^{-1}$ ) for each addition. NOTE: A1 and A3 have different time scales than A12 and A11. The symbol \* represents the  $\text{Br}^-$  and  $\text{NO}_3^-$  addition,  $\square$  represents the 1<sup>st</sup> glucose addition, and  $\bullet$  represents the 2<sup>nd</sup> glucose addition.

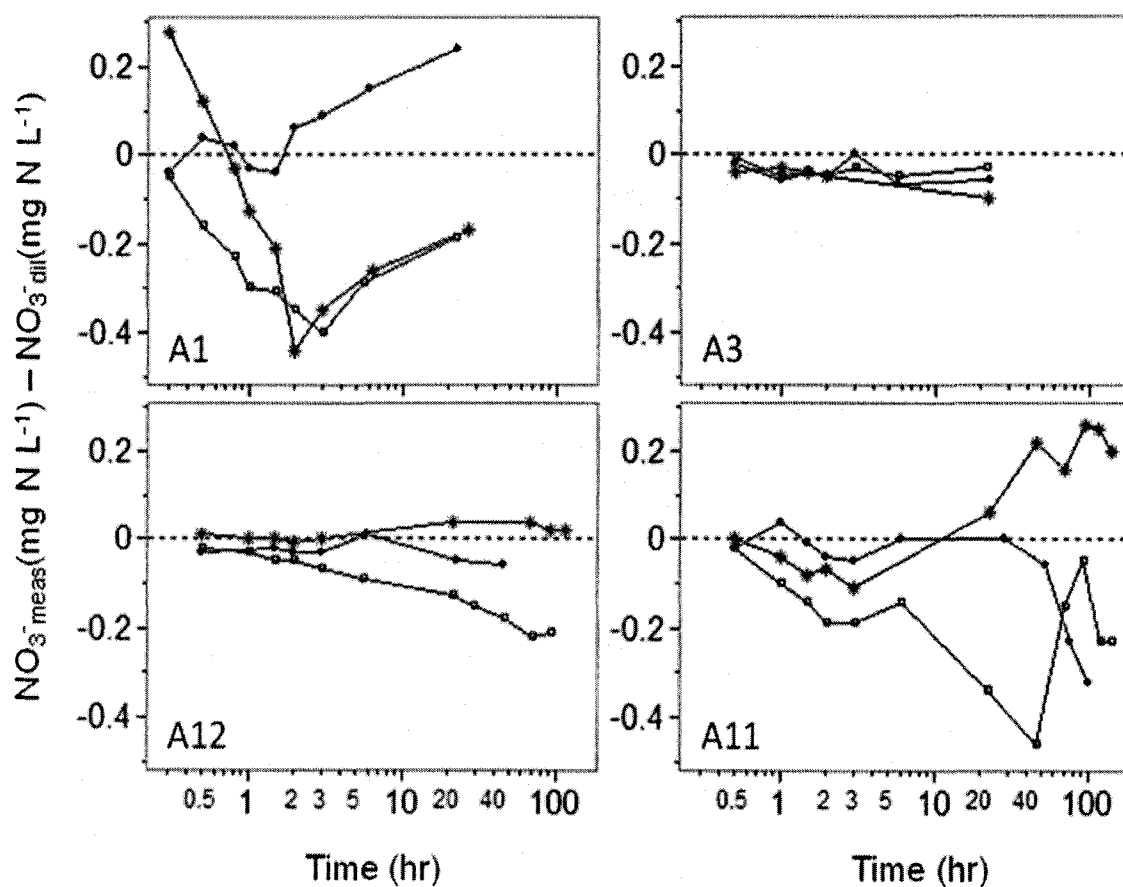


**Figure 11.** Dissolved organic carbon (DOC) concentrations (mg C L<sup>-1</sup>) for each addition. NOTE: A1 and A3 have different time scales than A12 and A11. The symbol \* represents the Br<sup>-</sup> and NO<sub>3</sub><sup>-</sup> addition and ■ represents the 1<sup>st</sup> glucose addition.

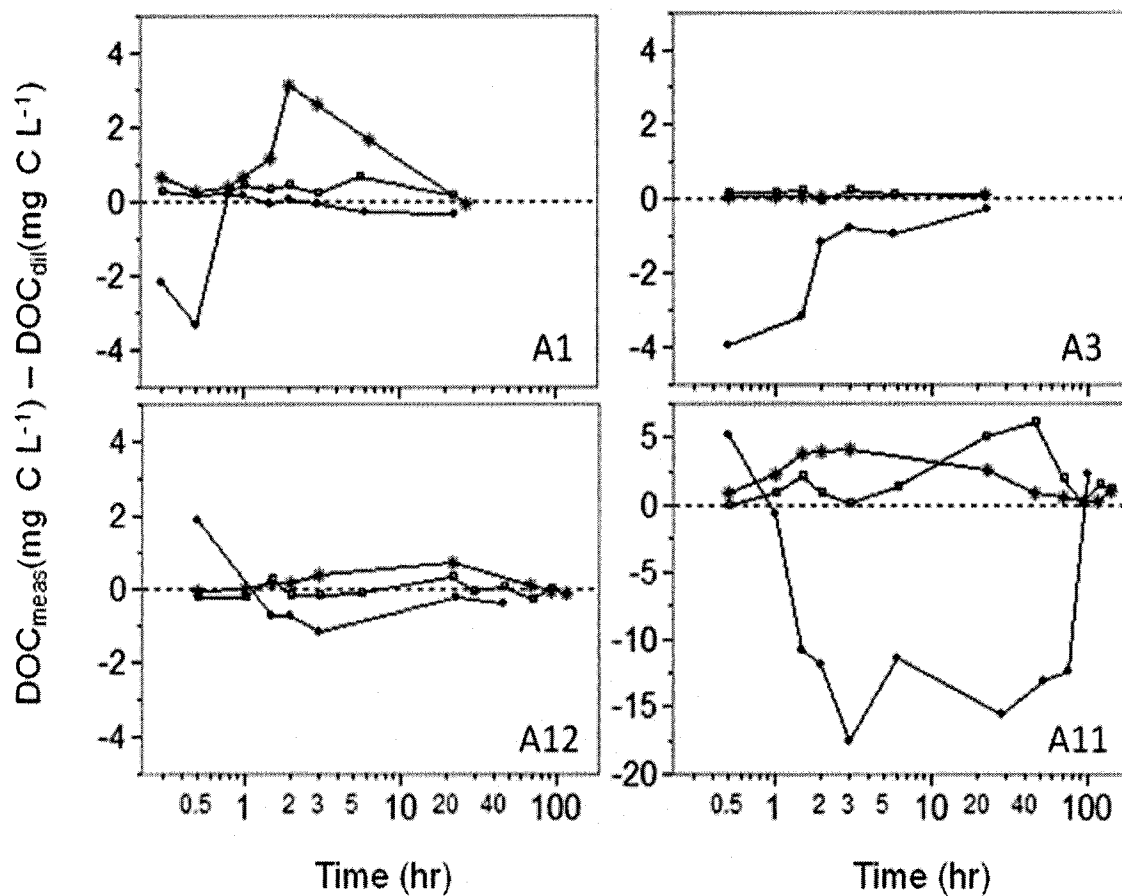


**Figure 12.** Dissolved organic carbon (DOC) concentrations ( $\text{mg C L}^{-1}$ ) during the 2<sup>nd</sup> glucose addition.

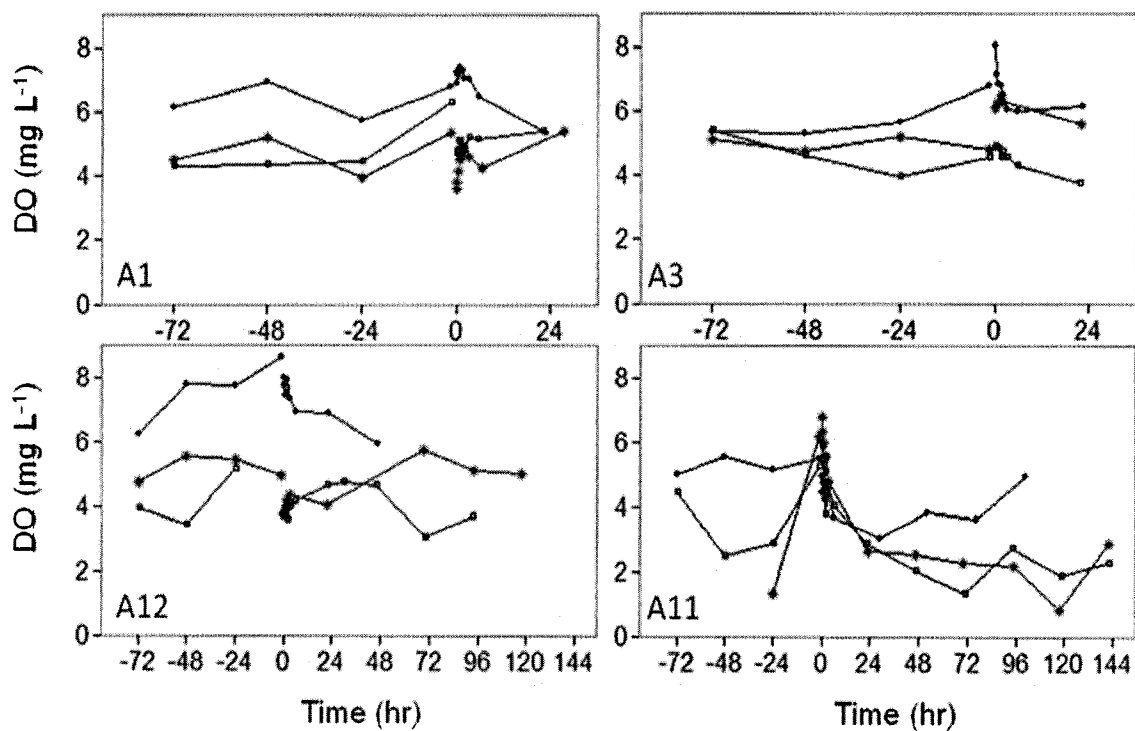




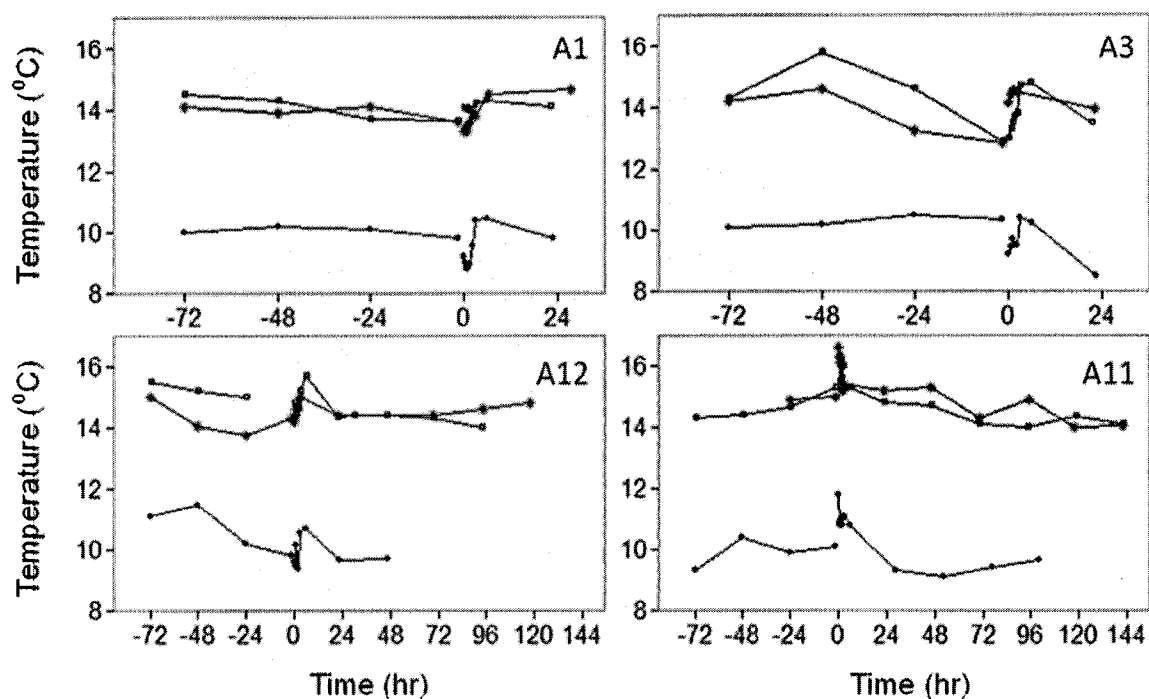
**Figure 13.** Nitrate ( $\text{NO}_3^-$ ) loss or  $\text{NO}_3^-$  production is defined if the data points are below or above the dotted line. The dotted line represents if  $\text{NO}_3^-$  was only being diluted away. The symbol \* represents the  $\text{Br}^-$  and  $\text{NO}_3^-$  addition,  $\square$  represents the 1<sup>st</sup> glucose addition, and  $\bullet$  represents the 2<sup>nd</sup> glucose addition.



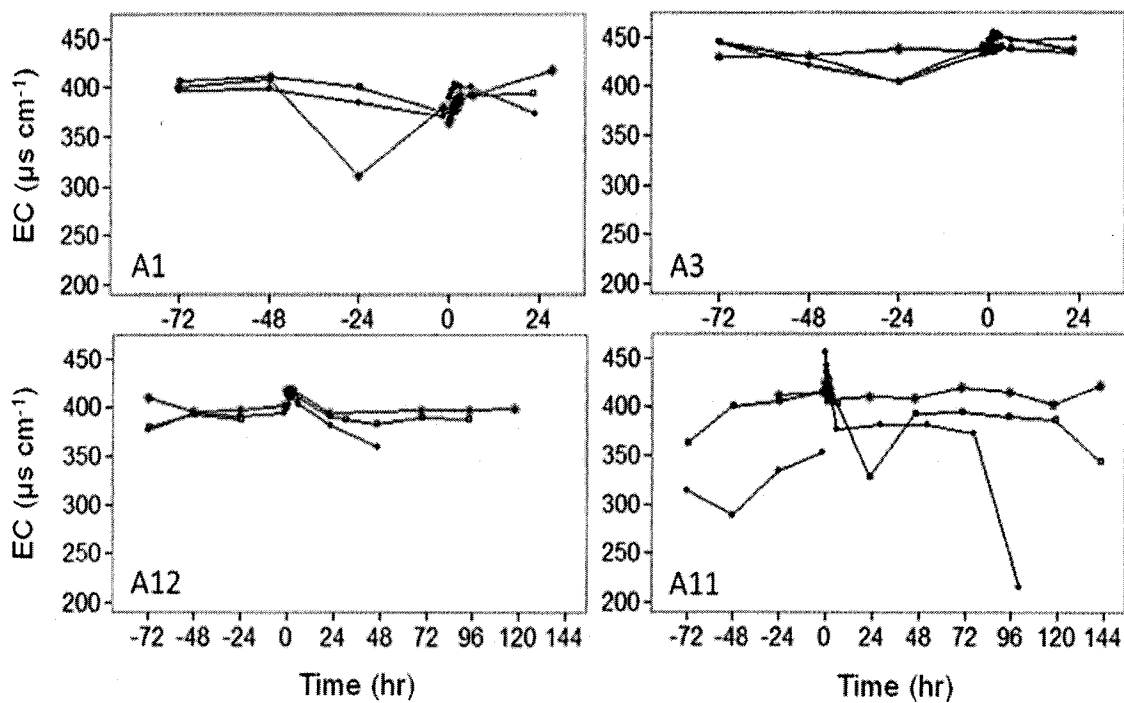
**Figure 14.** Dissolved organic carbon (DOC) loss or DOC production is defined if the data points are below or above the dotted line. The dotted line represents if DOC was only being diluted away. Note: A11 DOC scale is different from A1, A12, and A3. The symbol \* represents the Br<sup>-</sup> and NO<sub>3</sub><sup>-</sup> addition, ■ represents the 1<sup>st</sup> glucose addition, and ● represents the 2<sup>nd</sup> glucose addition.



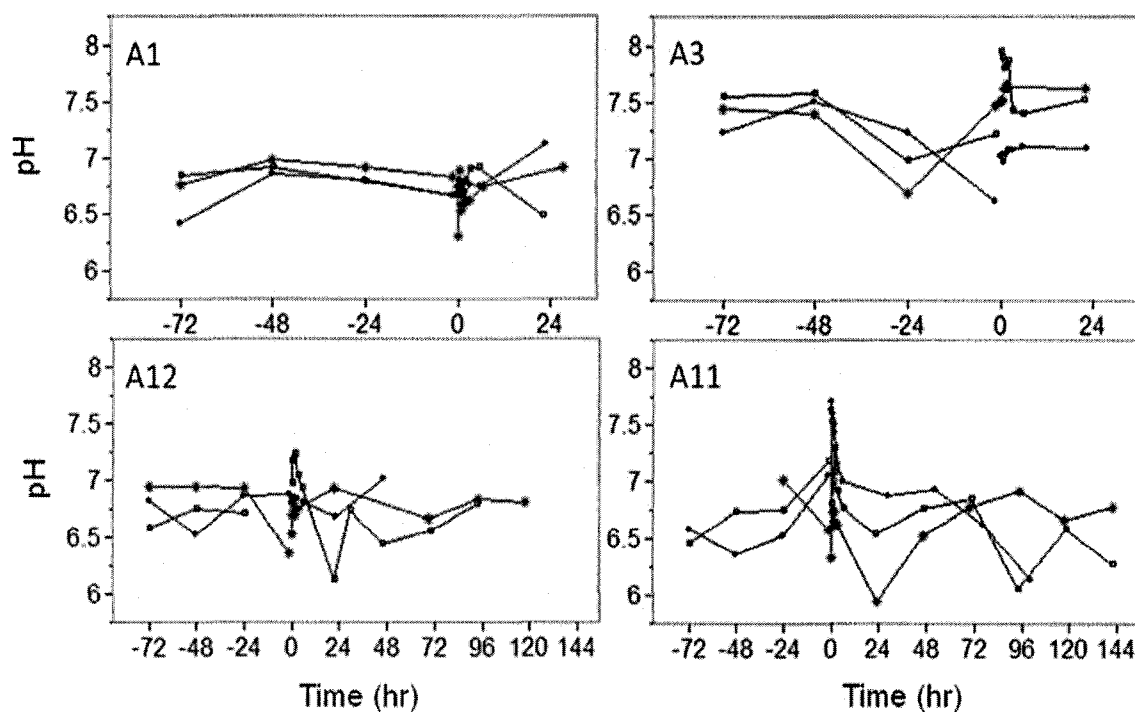
**Figure 15.** Ambient groundwater dissolved oxygen (DO) concentrations (mg L<sup>-1</sup>) measured 3 days prior to and throughout the push phase of each addition. NOTE: A1 and A3 have different time scales than A12 and A11. The symbol \* represents the Br<sup>-</sup> and NO<sub>3</sub><sup>-</sup> addition, ■ represents the 1<sup>st</sup> glucose addition, and ● represents the 2<sup>nd</sup> glucose addition.



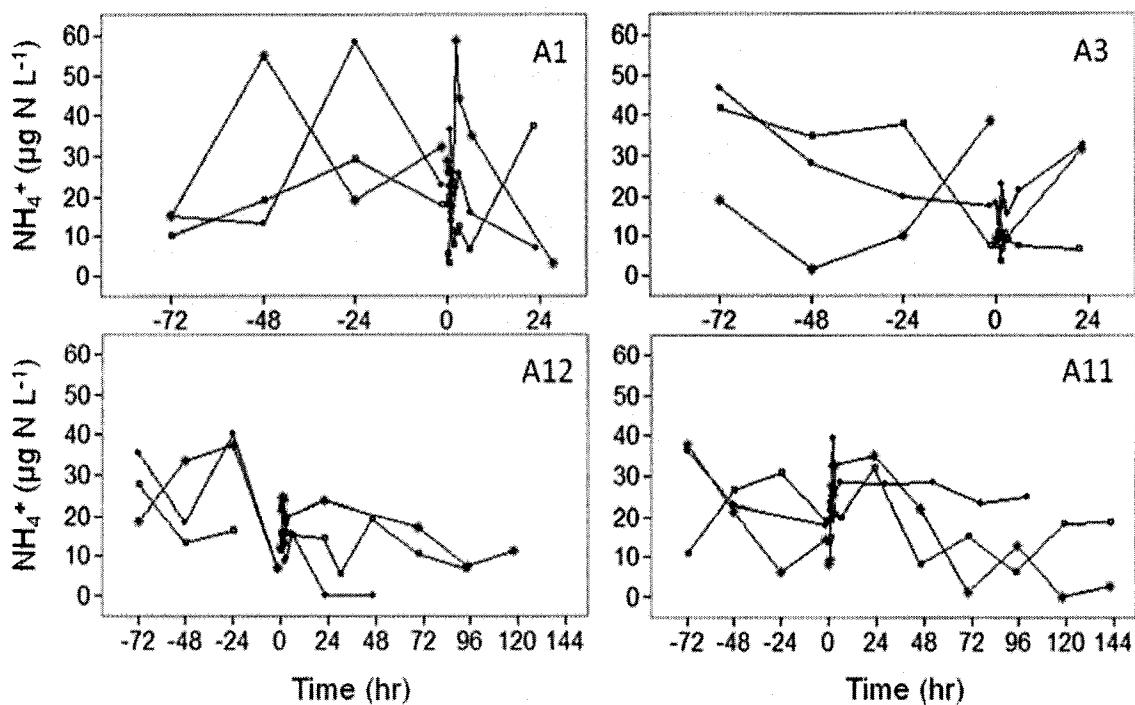
**Figure 16.** Ambient groundwater temperature (°C) measured 3 days prior to and throughout the push phase of each addition. NOTE: A1 and A3 have different time scales than A12 and A11. The symbol \* represents the  $\text{Br}^-$  and  $\text{NO}_3^-$  addition,  $\blacksquare$  represents the 1<sup>st</sup> glucose addition, and  $\bullet$  represents the 2<sup>nd</sup> glucose addition.



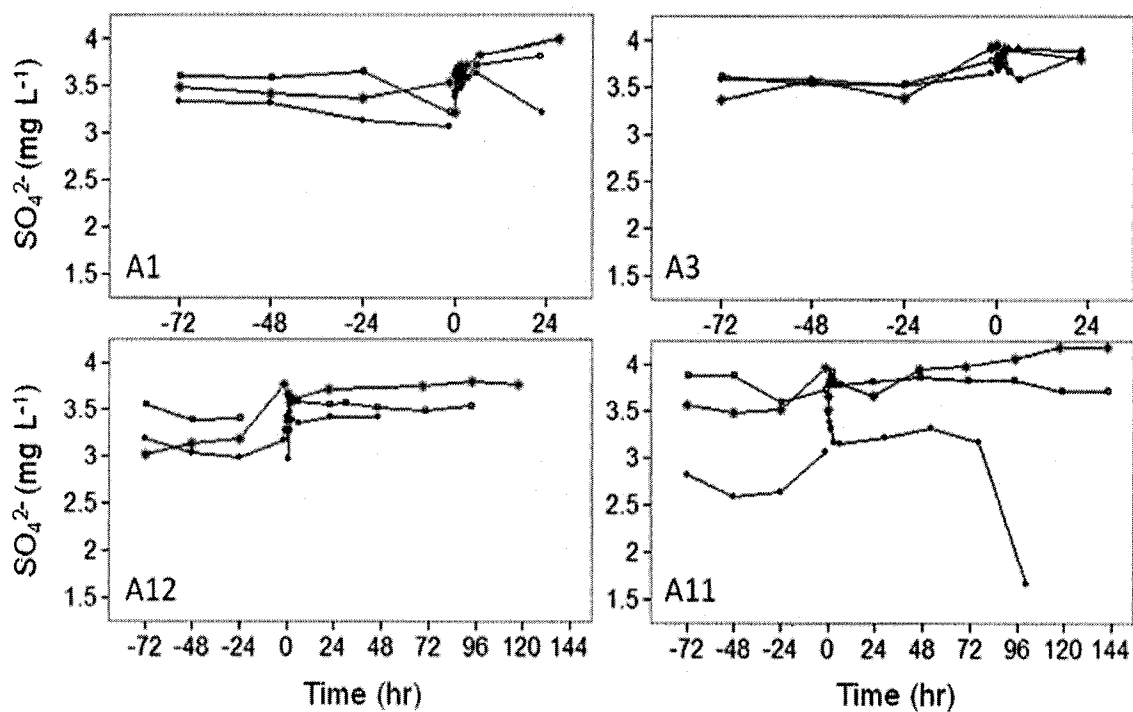
**Figure 17.** Ambient specific conductivity (EC) ( $\mu\text{S cm}^{-1}$ ) measured 3 days prior to and throughout the push phase of each addition. NOTE: A1 and A3 have different time scales than A12 and A11. The symbol \* represents the  $\text{Br}^-$  and  $\text{NO}_3^-$  addition,  $\blacksquare$  represents the 1<sup>st</sup> glucose addition, and  $\bullet$  represents the 2<sup>nd</sup> glucose addition.



**Figure 18.** Ambient pH measured 3 days prior to and throughout the push phase of each addition. NOTE: A1 and A3 have different time scales than A12 and A11. The symbol \* represents the  $\text{Br}^-$  and  $\text{NO}_3^-$  addition, ■ represents the 1<sup>st</sup> glucose addition, and ● represents the 2<sup>nd</sup> glucose addition.

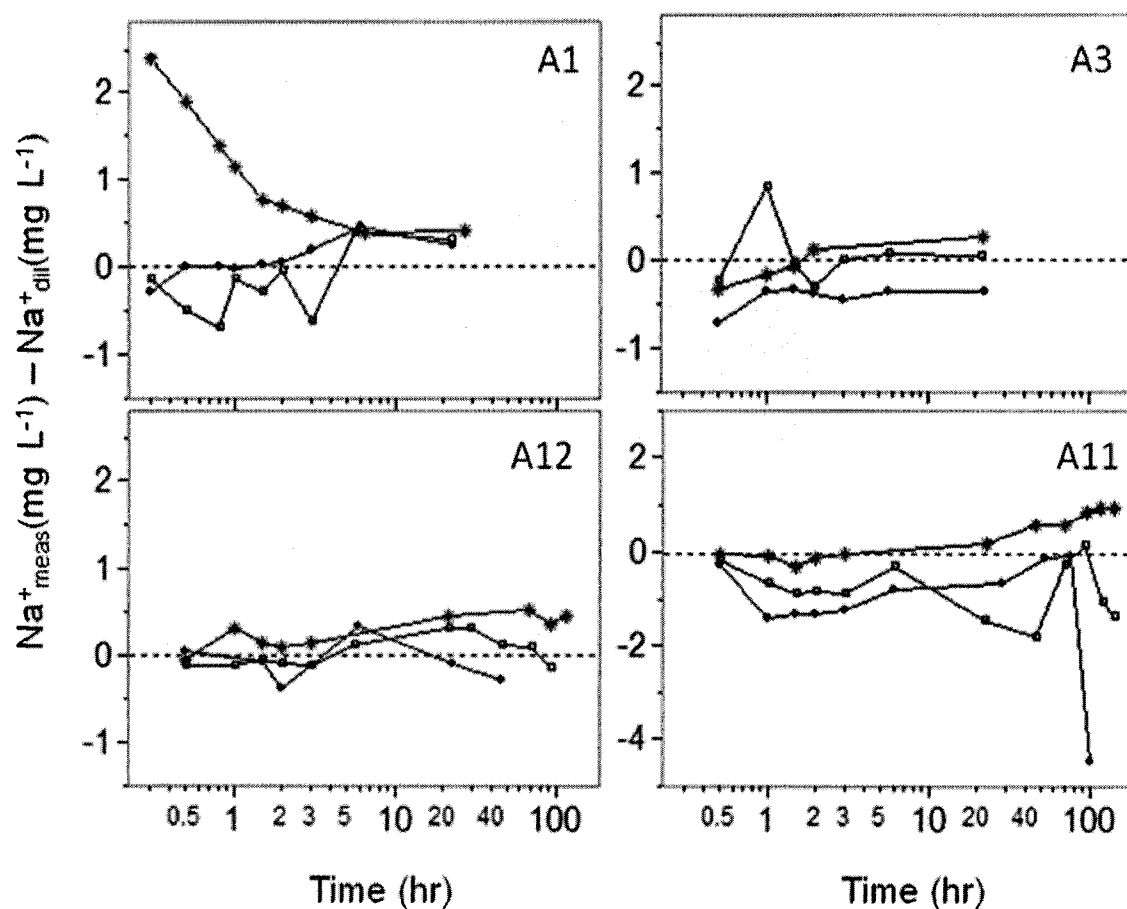


**Figure 19.** Ambient ammonium ( $\text{NH}_4^+$ ) concentrations ( $\text{mg N L}^{-1}$ ) measured 3 days prior to and throughout the push phase of each addition. NOTE: A1 and A3 have different time scales than A12 and A11. The symbol \* represents the  $\text{Br}^-$  and  $\text{NO}_3^-$  addition,  $\square$  represents the 1<sup>st</sup> glucose addition, and  $\bullet$  represents the 2<sup>nd</sup> glucose addition.



**Figure 20.** Ambient sulfate ( $\text{SO}_4^{2-}$ ) concentrations ( $\text{mg L}^{-1}$ ) measured 3 days prior to and throughout the push phase of each addition. NOTE: A1 and A3 have different time scales than A12 and A11. The symbol \* represents the  $\text{Br}^-$  and  $\text{NO}_3^-$  addition, ■ represents the 1<sup>st</sup> glucose addition, and ● represents the 2<sup>nd</sup> glucose addition.





**Figure 21.** Sodium ( $\text{Na}^+$ ) loss and  $\text{Na}^+$  production is defined if the data points are below or above the dotted line. The dotted line represents if  $\text{Na}^+$  was only being diluted away. NOTE: A11 has a different  $\text{Na}^+$  scale than A1, A12, and A3. The symbol \* represents the  $\text{Br}^-$  and  $\text{NO}_3^-$  addition,  $\square$  represents the 1<sup>st</sup> glucose addition, and  $\bullet$  represents the 2<sup>nd</sup> glucose addition.

## APPENDICES

# APPENDIX A

## Br<sup>-</sup> and NO<sub>3</sub><sup>-</sup> addition dissolved oxygen (DO), nitrate (NO<sub>3</sub><sup>-</sup>), ammonium (NH<sub>4</sub><sup>+</sup>), total dissolved nitrogen (TDN), and dissolved organic carbon (DOC) concentrations

UNH #	Well	Sample Name	Date	Time (hr)	DO (mg L <sup>-1</sup> )	NO <sub>3</sub> <sup>-</sup> (mg N L <sup>-1</sup> )	NH <sub>4</sub> <sup>+</sup> (μg N L <sup>-1</sup> )	TDN (mg N L <sup>-1</sup> )	DOC (mg C L <sup>-1</sup> )
62668	A11	A11-Ambient	09/05/06	-72	.	0.31	38	0.53	3.56
62669	A11	A11-Ambient	09/06/06	-48	.	0.57	22	0.80	1.30
62670	A11	A11-Ambient	09/07/06	-24	1.33	0.71	6	0.96	2.02
62680	A11	A11-Ambient	09/08/06	-1.5	6.22	0.54	15	0.96	1.65
62681	A11	A11-GW Soln	09/08/06	.	5.37	2.49	19	2.75	1.23
62682	A11	A11-Start	09/08/06	0	6.81	2.53	8	2.79	1.40
62683	A11	A11-Leftover	09/08/06	0	.	2.53	1	2.77	1.35
62684	A11	A11-1	09/08/06	0.5	6.36	2.48	10	2.79	2.39
62685	A11	A11-2	09/08/06	1	5.98	2.36	9	2.72	3.76
62686	A11	A11-3	09/08/06	1.5	5.53	2.06	28	2.50	5.28
62687	A11	A11-4	09/08/06	2	5.58	1.88	25	2.32	5.49
62688	A11	A11-5	09/08/06	3	4.82	1.66	33	2.13	5.67
62689	A11	A11-6	09/09/06	22.7	2.67	1.52	35	1.90	4.16
62690	A11	A11-7	09/10/06	46.1	2.57	1.32	22	1.56	2.50
62691	A11	A11-8	09/11/06	70.2	2.29	1.08	0	1.25	2.24
62692	A11	A11-9	09/12/06	94.8	2.22	1.06	13	1.23	1.87
62693	A11	A11-10	09/13/06	117.8	0.83	0.99	0	1.15	1.97
62694	A11	A11-11	09/14/06	142	2.89	0.88	3	1.00	2.68
62671	A1	A1-Ambient	09/10/06	-72	4.52	2.29	15	2.62	0.41
62672	A1	A1-Ambient	09/11/06	-48	5.18	2.30	55	2.59	0.54

UNH #	Well	Sample Name	Date	Time (hr)	DO (mg L <sup>-1</sup> )	NO <sub>3</sub> <sup>-</sup> (mg N L <sup>-1</sup> )	NH <sub>4</sub> <sup>+</sup> (µg N L <sup>-1</sup> )	TDN (mg N L <sup>-1</sup> )	DOC (mg C L <sup>-1</sup> )
62673	A1	A1-Ambient	09/12/06	-24	3.94	2.31	19	2.79	0.56
62695	A1	A1-Ambient	09/13/06	-1.5	5.35	2.30	32	2.09	0.61
62696	A1	A1-GW Soln	09/13/06	.	6.01	3.13	31	3.55	0.83
62697	A1	A1-Start	09/13/06	0	3.61	2.68	29	2.86	0.55
62698	A1	A1-Leftover	09/13/06	0	.	2.80	25	3.31	0.85
62699	A1	A1-1	09/13/06	0.3	3.81	2.97	26	3.19	1.21
62700	A1	A1-2	09/13/06	0.5	4.16	2.75	26	3.26	0.82
62701	A1	A1-3	09/13/06	0.8	4.51	2.52	26	2.92	0.96
62702	A1	A1-4	09/13/06	1	4.67	2.38	21	2.59	1.26
62703	A1	A1-5	09/13/06	1.5	4.93	2.25	24	2.72	1.73
62704	A1	A1-6	09/13/06	2	4.75	1.99	59	2.85	3.73
62705	A1	A1-7	09/13/06	3	4.61	2.05	44	2.58	3.20
62706	A1	A1-8	09/13/06	6.4	4.25	2.09	35	2.56	2.29
62707	A1	A1-9	09/14/06	22.6	5.21	1.69	16	1.91	0.36
62708	A1	A1-10	09/14/06	27.3	5.39	2.14	3	2.18	0.53
62709	A1	A1-11	09/15/06	46.9	5.57	2.19	15	2.52	0.22
63419	A1	A1-12	09/16/06	71	5.82	2.24	5	2.42	0.21
63420	A1	A1-13	09/17/06	94.6	5.24	2.23	15	2.02	0.45
63421	A1	A1-14	09/18/06	118.4	5.59	2.40	33	2.43	0.40
62674	A3	A3-Ambient	09/07/06	-72	5.12	1.54	19	1.61	0.33
62675	A3	A3-Ambient	09/08/06	-48	4.75	1.56	2	1.69	0.34
62676	A3	A3-Ambient	09/09/06	-24	5.20	1.61	10	1.75	0.52
62710	A3	A3-Ambient	09/10/06	-1.5	4.81	1.55	39	1.64	0.52
62711	A3	A3-GW Soln	09/10/06	.	6.35	2.76	4	2.99	0.41
62712	A3	A3-Start	09/10/06	0	6.12	2.79	9	3.07	0.50
62713	A3	A3-Leftover	09/10/06	0	.	2.82	7	3.01	0.59
62714	A3	A3-1	09/10/06	0.5	6.18	2.55	10	2.82	0.56
62715	A3	A3-2	09/10/06	1	6.30	2.39	17	2.65	0.56
62716	A3	A3-3	09/10/06	1.5	6.52	2.15	10	2.39	0.59

UNH #	Well	Sample Name	Date	Time (hr)	DO (mg L <sup>-1</sup> )	NO <sub>3</sub> <sup>-</sup> (mg N L <sup>-1</sup> )	NH <sub>4</sub> <sup>+</sup> (µg N L <sup>-1</sup> )	TDN (mg N L <sup>-1</sup> )	DOC (mg C L <sup>-1</sup> )
62717	A3	A3-4	09/10/06	2	6.28	1.98	9	2.19	0.57
62718	A3	A3-5	09/10/06	3	6.21	2.13	20	2.07	0.66
62719	A3	A3-6	09/11/06	22.1	5.62	1.46	31	1.65	0.62
62720	A3	A3-7	09/12/06	46.6	4.23	1.47	7	1.60	0.38
62721	A3	A3-8	09/13/06	69.7	4.26	1.47	14	1.60	0.50
62722	A3	A3-9	09/14/06	93.9	5.48	1.45	23	1.61	0.47
62723	A3	A3-10	09/15/06	117.3	5.60	1.47	28	1.63	0.50
62724	A3	A3-11	09/16/06	142.4	5.50	1.47	5	1.58	0.36
62677	A12	A12-Ambient	09/09/06	-72	4.75	1.86	19	1.73	0.54
62678	A12	A12-Ambient	09/10/06	-48	5.53	2.11	34	2.42	0.75
62679	A12	A12-Ambient	09/11/06	-24	5.44	2.01	38	2.53	0.71
62725	A12	A12-Ambient	09/12/06	-1.5	4.96	1.97	7	2.11	0.42
62726	A12	A12-GW Soln	09/12/06	.	4.63	3.14	13	3.44	0.96
62727	A12	A12-Start	09/12/06	0	3.78	3.13	12	3.44	0.89
62728	A12	A12-Leftover	09/12/06	0	.	3.02	18	3.34	0.86
62729	A12	A12-1	09/12/06	0.5	3.77	3.10	21	3.37	0.82
62730	A12	A12-2	09/12/06	1	3.89	3.01	24	3.23	0.84
62731	A12	A12-3	09/12/06	1.5	4.06	2.89	24	3.19	0.97
62732	A12	A12-4	09/12/06	2	4.19	2.79	13	3.09	0.94
62733	A12	A12-5	09/12/06	3	4.37	2.68	20	3.00	1.11
62734	A12	A12-6	09/13/06	21.7	4.07	2.27	24	2.55	1.25
62735	A12	A12-7	09/13/06	29.8	3.80	2.31	22	2.53	1.33
62736	A12	A12-8	09/14/06	45.9	5.14	1.70	0	1.60	0.45
62737	A12	A12-9	09/15/06	69.2	5.75	2.05	17	2.22	0.54
62738	A12	A12-10	09/16/06	94.3	5.09	2.01	7	2.17	0.35
62739	A12	A12-11	09/17/06	117.8	5.02	2.01	11	2.20	0.33

## APPENDIX B

**Br<sup>-</sup> and NO<sub>3</sub><sup>-</sup> addition pH, specific conductivity (EC), bromide (Br<sup>-</sup>), sodium (Na<sup>+</sup>), and sulfate (SO<sub>4</sub><sup>2-</sup>) concentrations**

UNH #	Well	Sample Name	Date	Time (hr)	pH	EC ( $\mu\text{S cm}^{-1}$ )	Br <sup>-</sup> (mg L <sup>-1</sup> )	Na <sup>+</sup> (mg L <sup>-1</sup> )	SO <sub>4</sub> <sup>2-</sup> (mg L <sup>-1</sup> )
62668	A11	A11-Ambient	09/05/06	-72	.	.	0.14	14.13	3.56
62669	A11	A11-Ambient	09/06/06	-48	.	.	0.00	15.25	3.49
62670	A11	A11-Ambient	09/07/06	-24	7.02	411	0.00	15.86	3.51
62680	A11	A11-Ambient	09/08/06	-1.5	6.58	415	0.05	16.21	3.96
62681	A11	A11-GW Soln	09/08/06	.	6.65	432	6.56	20.00	3.46
62682	A11	A11-Start	09/08/06	0	6.34	424	6.70	20.12	3.52
62683	A11	A11-Leftover	09/08/06	0	.	.	6.71	20.14	3.59
62684	A11	A11-1	09/08/06	0.5	6.6	420	6.56	20.02	3.66
62685	A11	A11-2	09/08/06	1	6.73	415	6.28	19.77	3.80
62686	A11	A11-3	09/08/06	1.5	6.73	422	5.41	18.89	3.82
62687	A11	A11-4	09/08/06	2	6.65	419	4.77	18.62	3.85
62688	A11	A11-5	09/08/06	3	6.62	407	4.16	18.26	3.82
62689	A11	A11-6	09/09/06	22.7	5.94	410	3.13	17.75	3.67
62690	A11	A11-7	09/10/06	46.1	6.53	409	1.95	17.31	3.95
62691	A11	A11-8	09/11/06	70.2	6.78	420	1.32	16.87	3.98
62692	A11	A11-9	09/12/06	94.8	6.92	414	0.94	16.86	4.07
62693	A11	A11-10	09/13/06	117.8	6.66	402	0.71	16.77	4.18
62694	A11	A11-11	09/14/06	142	6.78	421	0.49	16.62	4.18
62671	A1	A1-Ambient	09/10/06	-72	6.77	401	0.07	17.50	3.49
62672	A1	A1-Ambient	09/11/06	-48	6.98	408	0.11	17.96	3.41
62673	A1	A1-Ambient	09/12/06	-24	6.91	310	0.09	18.03	3.37

UNH #	Well	Sample Name	Date	Time (hr)	pH	EC ( $\mu\text{S cm}^{-1}$ )	Br <sup>-</sup> (mg L <sup>-1</sup> )	Na <sup>+</sup> (mg L <sup>-1</sup> )	SO <sub>4</sub> <sup>2-</sup> (mg L <sup>-1</sup> )
62695	A1	A1-Ambient	09/13/06	-1.5	6.83	380	0.09	17.17	3.53
62696	A1	A1-GW Soln	09/13/06	.	7.09	402	6.67	20.98	3.64
62697	A1	A1-Start	09/13/06	0	6.3	363	5.71	18.21	3.21
62698	A1	A1-Leftover	09/13/06	0	.	.	5.97	19.02	3.28
62699	A1	A1-1	09/13/06	0.3	6.74	367	5.87	20.61	3.63
62700	A1	A1-2	09/13/06	0.5	6.89	375	4.85	20.02	3.62
62701	A1	A1-3	09/13/06	0.8	6.53	381	3.82	19.40	3.67
62702	A1	A1-4	09/13/06	1	6.58	383	3.14	19.11	3.68
62703	A1	A1-5	09/13/06	1.5	6.58	386	2.38	18.65	3.71
62704	A1	A1-6	09/13/06	2	6.62	390	1.93	18.54	3.59
62705	A1	A1-7	09/13/06	3	6.63	393	1.53	18.39	3.71
62706	A1	A1-8	09/13/06	6.4	6.75	393	0.80	18.13	3.83
62707	A1	A1-9	09/14/06	22.6	6.83	419	0.12	18.16	3.99
62708	A1	A1-10	09/14/06	27.3	6.91	418	0.12	18.09	4.00
62709	A1	A1-11	09/15/06	46.9	6.7	416	0.09	18.04	4.01
63419	A1	A1-12	09/16/06	71	6.93	417	0.08	17.96	4.02
63420	A1	A1-13	09/17/06	94.6	6.86	418	0.09	17.93	4.04
63421	A1	A1-14	09/18/06	118.4	7.02	419	0.15	17.85	3.67
62674	A3	A3-Ambient	09/07/06	-72	7.44	431	0.00	17.15	3.37
62675	A3	A3-Ambient	09/08/06	-48	7.4	432	0.07	17.37	3.56
62676	A3	A3-Ambient	09/09/06	-24	6.7	438	0.00	17.50	3.39
62710	A3	A3-Ambient	09/10/06	-1.5	7.47	437	0.04	17.83	3.94
62711	A3	A3-GW Soln	09/10/06	.	7.5	461	6.25	21.57	3.73
62712	A3	A3-Start	09/10/06	0	7.52	442	6.39	21.85	3.95
62713	A3	A3-Leftover	09/10/06	0	.	.	6.56	21.89	3.80
62714	A3	A3-1	09/10/06	0.5	7.53	447	5.39	20.84	3.81
62715	A3	A3-2	09/10/06	1	7.63	450	4.53	20.40	3.83
62716	A3	A3-3	09/10/06	1.5	7.67	452	3.34	19.69	3.87
62717	A3	A3-4	09/10/06	2	7.64	451	2.52	19.30	3.92

UNH #	Well	Sample Name	Date	Time (hr)	pH	EC ( $\mu\text{S cm}^{-1}$ )	Br <sup>-</sup> (mg L <sup>-1</sup> )	Na <sup>+</sup> (mg L <sup>-1</sup> )	SO <sub>4</sub> <sup>2-</sup> (mg L <sup>-1</sup> )
62718	A3	A3-5	09/10/06	3	7.7	450	0.05	18.98	3.87
62719	A3	A3-6	09/11/06	22.1	7.63	437	0.13	17.79	3.80
62720	A3	A3-7	09/12/06	46.6	7.42	433	0.13	17.48	3.85
62721	A3	A3-8	09/13/06	69.7	7.34	430	0.09	17.57	3.98
62722	A3	A3-9	09/14/06	93.9	7.52	444	0.11	17.60	4.01
62723	A3	A3-10	09/15/06	117.3	7.48	445	0.08	17.82	4.02
62724	A3	A3-11	09/16/06	142.4	7.6	446	0.08	17.69	4.02
62677	A12	A12-Ambient	09/09/06	-72	6.94	410	0.00	16.63	3.02
62678	A12	A12-Ambient	09/10/06	-48	6.94	396	0.10	17.34	3.14
62679	A12	A12-Ambient	09/11/06	-24	6.93	397	0.00	17.54	3.19
62725	A12	A12-Ambient	09/12/06	-1.5	6.36	402	0.05	17.52	3.77
62726	A12	A12-GW Soln	09/12/06	.	7.04	409	6.39	21.04	3.62
62727	A12	A12-Start	09/12/06	0	6.53	418	6.41	20.74	3.26
62728	A12	A12-Leftover	09/12/06	0	.	.	6.13	20.07	3.18
62729	A12	A12-1	09/12/06	0.5	6.69	413	6.19	20.58	3.28
62730	A12	A12-2	09/12/06	1	6.79	416	5.72	20.70	3.66
62731	A12	A12-3	09/12/06	1.5	6.69	419	5.09	20.16	3.63
62732	A12	A12-4	09/12/06	2	6.74	417	4.55	19.82	3.57
62733	A12	A12-5	09/12/06	3	6.75	418	3.91	19.53	3.62
62734	A12	A12-6	09/13/06	21.7	6.93	394	1.45	18.49	3.72
62735	A12	A12-7	09/13/06	29.8	6.84	394	1.60	18.86	3.77
62736	A12	A12-8	09/14/06	45.9	6.74	399	0.47	18.49	3.80
62737	A12	A12-9	09/15/06	69.2	6.66	397	0.22	17.89	3.75
62738	A12	A12-10	09/16/06	94.3	6.83	398	0.13	17.68	3.80
62739	A12	A12-11	09/17/06	117.8	6.8	399	0.10	17.76	3.77



## APPENDIX C

**1<sup>ST</sup> glucose addition dissolved oxygen (DO), nitrate (NO<sub>3</sub><sup>-</sup>), ammonium (NH<sub>4</sub><sup>+</sup>),  
total dissolved nitrogen (TDN), and dissolved organic carbon (DOC) concentrations**

UNH #	Well	Sample Name	Date	Time (hr)	DO (mg L <sup>-1</sup> )	NO <sub>3</sub> <sup>-</sup> (mg N L <sup>-1</sup> )	NH <sub>4</sub> <sup>+</sup> (μg N L <sup>-1</sup> )	TDN (mg N L <sup>-1</sup> )	DOC (mg C L <sup>-1</sup> )
63407	A11	A11-Ambient	09/16/06	-72	4.44	0.31	11	0.48	3.82
63408	A11	A11-Ambient	09/17/06	-48	2.48	0.38	27	0.54	2.84
63409	A11	A11-Ambient	09/18/06	-24	2.88	0.64	31	-0.02	1.89
63329	A11	A11-Ambient	09/19/06	-1.5	5.26	0.49	19	0.65	3.36
63330	A11	A11-GW Soln	09/19/06	.	5.23	2.58	10	2.74	3.05
63331	A11	A11-Start	09/19/06	0	5.91	2.57	13	2.80	2.92
63332	A11	A11-Leftover	09/19/06	0	.	2.57	11	2.76	2.88
63333	A11	A11-1	09/19/06	0.5	5.43	2.55	15	2.80	2.92
63334	A11	A11-2	09/19/06	1	5.29	2.37	19	2.66	3.89
63335	A11	A11-3	09/19/06	1.5	5.08	2.04	27	2.37	5.10
63336	A11	A11-4	09/19/06	2	3.82	1.79	27	2.07	3.99
63337	A11	A11-5	09/19/06	3	4.67	1.52	21	1.71	3.32
63338	A11	A11-6	09/19/06	6.1	4.04	1.31	20	1.54	4.52
63339	A11	A11-7	09/20/06	22.4	2.89	0.64	32	0.83	8.24
63340	A11	A11-8	09/21/06	46.3	2.05	0.44	8	0.56	9.45
63341	A11	A11-9	09/22/06	70.3	1.33	0.68	15	0.79	5.36
63342	A11	A11-10	09/23/06	94.3	2.75	0.64	6	0.69	3.46
63343	A11	A11-11	09/24/06	118.3	1.92	0.34	18	0.37	4.89
63530	A11	A11-12	09/25/06	142.1	2.30	0.33	19	0.45	4.55
63410	A3	A3-Ambient	09/18/06	-72	5.40	1.51	42	1.64	0.52

UNH #	Well	Sample Name	Date	Time (hr)	DO (mg L <sup>-1</sup> )	NO <sub>3</sub> <sup>-</sup> (mg N L <sup>-1</sup> )	NH <sub>4</sub> <sup>+</sup> (μg N L <sup>-1</sup> )	TDN (mg N L <sup>-1</sup> )	DOC (mg C L <sup>-1</sup> )
63411	A3	A3-Ambient	09/19/06	-48	4.61	1.50	35	1.70	0.56
63412	A3	A3-Ambient	09/20/06	-24	3.94	1.51	38	1.68	0.29
63344	A3	A3-Ambient	09/21/06	-1.5	4.57	1.49	7	1.65	0.45
63345	A3	A3-GW Soln	09/21/06	.	4.53	2.78	17	3.08	3.08
63346	A3	A3-Start	09/21/06	0	4.91	2.79	7	3.11	3.04
63347	A3	A3-Leftover	09/21/06	0.1	.	2.42	7	2.72	2.64
63348	A3	A3-1	09/21/06	0.5	4.85	2.58	10	2.87	2.80
63349	A3	A3-2	09/21/06	1	4.83	2.30	4	2.52	2.31
63350	A3	A3-3	09/21/06	1.5	4.53	2.04	7	2.30	1.86
63351	A3	A3-4	09/21/06	2	4.77	1.86	11	2.08	1.26
63352	A3	A3-5	09/21/06	3	4.56	1.69	9	1.87	1.13
63353	A3	A3-6	09/21/06	5.7	4.32	1.54	7	1.70	0.75
63354	A3	A3-7	09/22/06	21.5	3.73	1.46	7	1.56	0.55
63355	A3	A3-8	09/23/06	45.5	5.55	1.45	9	1.55	0.41
63356	A3	A3-9	09/24/06	69.6	5.11	1.45	9	1.56	0.42
63357	A3	A3-10	09/25/06	93.3	4.16	1.43	4	1.52	0.36
63358	A3	A3-11	09/26/06	117.4	4.17	1.44	5	1.54	0.34
63526	A3	A3-12	09/27/06	141.5	3.93	1.62	7	1.45	0.48
63413	A12	A12-Ambient	09/21/06	-72	3.93	2.09	28	2.36	0.25
63414	A12	A12-Ambient	09/20/06	-48	3.47	2.10	13	2.05	0.50
63415	A12	A12-Ambient	09/21/06	-24	5.17	2.11	17	2.43	0.32
63359	A12	A12-Ambient	09/22/06	-1.5	4.33	2.10	17	2.04	0.44
63360	A12	A12-GW Soln	09/22/06	.	3.84	3.15	21	3.41	3.38
63361	A12	A12-Start	09/22/06	0	3.91	3.15	15	3.36	3.38
63362	A12	A12-Leftover	09/22/06	0.1	.	3.15	20	3.39	3.14
63363	A12	A12-1	09/22/06	0.5	3.72	3.07	14	3.28	2.97
63364	A12	A12-2	09/22/06	1	3.76	2.98	13	2.99	2.76
63365	A12	A12-3	09/22/06	1.5	3.97	2.85	25	3.13	2.98
63366	A12	A12-4	09/22/06	2	3.62	2.72	19	2.96	2.13

UNH #	Well	Sample Name	Date	Time (hr)	DO (mg L <sup>-1</sup> )	NO <sub>3</sub> <sup>-</sup> (mg N L <sup>-1</sup> )	NH <sub>4</sub> <sup>+</sup> (µg N L <sup>-1</sup> )	TDN (mg N L <sup>-1</sup> )	DOC (mg C L <sup>-1</sup> )
63367	A12	A12-5	09/22/06	3	4.01	2.61	16	2.83	1.89
63368	A12	A12-6	09/22/06	5.6	4.14	2.52	15	2.76	1.75
63369	A12	A12-7	09/23/06	21.8	4.63	2.16	15	2.18	1.31
63370	A12	A12-8	09/23/06	29.6	4.73	2.09	5	2.30	0.78
63371	A12	A12-9	09/24/06	45.9	4.67	1.98	19	2.15	0.63
63372	A12	A12-10	09/25/06	69.6	3.07	1.90	11	2.10	0.23
63373	A12	A12-11	09/26/06	93.7	3.69	1.91	7	2.12	0.50
63527	A12	A12-12	09/27/06	117.8	3.77	1.89	12	2.08	0.50
63416	A1	A1-Ambient	09/20/06	-72	4.29	2.27	10	2.47	0.16
63417	A1	A1-Ambient	09/21/06	-48	4.35	2.29	19	2.59	0.27
63418	A1	A1-Ambient	09/22/06	-24	4.46	2.29	29	2.71	0.25
63374	A1	A1-Ambient	09/23/06	-1.5	6.31	2.28	18	1.49	0.22
63375	A1	A1-GW Soln	09/23/06	.	5.72	3.09	4	3.25	2.53
63376	A1	A1-Start	09/23/06	0	4.82	2.95	5	2.96	2.46
63377	A1	A1-Leftover	09/23/06	0	.	2.53	5	2.73	2.24
63378	A1	A1-1	09/23/06	0.3	4.76	2.79	3	2.89	2.39
63379	A1	A1-2	09/23/06	0.5	5.08	2.54	14	2.76	1.79
63380	A1	A1-3	09/23/06	0.8	5.11	2.39	16	2.44	1.56
63381	A1	A1-4	09/23/06	1	4.97	2.25	11	2.35	1.56
63382	A1	A1-5	09/23/06	1.5	4.89	2.16	8	2.39	1.17
63383	A1	A1-6	09/23/06	2	4.82	2.08	11	2.29	1.12
63384	A1	A1-7	09/23/06	3	5.18	2.00	13	1.87	0.83
63385	A1	A1-8	09/23/06	5.6	5.16	2.00	7	2.25	0.93
63386	A1	A1-9	09/24/06	22	5.42	2.11	37	2.19	0.45
63387	A1	A1-10	09/24/06	29.7	5.74	2.01	20	2.30	0.35
63388	A1	A1-11	09/25/06	45.6	3.93	2.10	2	2.31	0.48
63389	A1	A1-12	09/26/06	69.8	3.69	2.11	3	2.29	0.27
63390	A1	A1-13	09/27/06	93.9	4.76	2.11	13	2.30	0.28
63528	A1	A1-14	09/28/06	118.1	5.88	2.12	10	2.21	0.35

## APPENDIX D

1<sup>st</sup> glucose addition pH, specific conductivity (EC), bromide (Br<sup>-</sup>), sodium (Na<sup>+</sup>), and sulfate (SO<sub>4</sub><sup>2-</sup>) concentrations

UNH #	Well	Sample Name	Date	Time (hr)	pH	EC ( $\mu\text{s cm}^{-1}$ )	Br <sup>-</sup> (mg L <sup>-1</sup> )	Na <sup>+</sup> (mg L <sup>-1</sup> )	SO <sub>4</sub> <sup>2-</sup> (mg L <sup>-1</sup> )
63407	A11	A11-Ambient	09/16/06	-72	6.46	362	0.28	14.93	3.89
63408	A11	A11-Ambient	09/17/06	-48	6.74	401	0.22	15.36	3.88
63409	A11	A11-Ambient	09/18/06	-24	6.75	406	0.16	16.22	3.60
63329	A11	A11-Ambient	09/19/06	-1.5	7.18	415	0.21	16.32	3.74
63330	A11	A11-GW Soln	09/19/06	.	7.26	436	7.05	21.20	3.79
63331	A11	A11-Start	09/19/06	0	7.53	435	6.37	21.06	3.79
63332	A11	A11-Leftover	09/19/06	0	.	.	6.37	21.02	3.78
63333	A11	A11-1	09/19/06	0.5	6.81	407	6.37	20.88	3.79
63334	A11	A11-2	09/19/06	1	6.96	405	6.08	20.18	3.87
63335	A11	A11-3	09/19/06	1.5	7.29	426	5.24	19.20	3.91
63336	A11	A11-4	09/19/06	2	7.09	409	4.63	18.70	3.87
63337	A11	A11-5	09/19/06	3	6.92	410	3.82	18.00	3.78
63338	A11	A11-6	09/19/06	6.1	6.77	404	3.08	17.89	3.79
63339	A11	A11-7	09/20/06	22.4	6.54	328	1.66	15.54	3.81
63340	A11	A11-8	09/21/06	46.3	6.77	393	1.43	14.96	3.87
63341	A11	A11-9	09/22/06	70.3	6.85	395	1.22	16.34	3.84
63342	A11	A11-10	09/23/06	94.3	6.06	389	0.81	16.39	3.84
63343	A11	A11-11	09/24/06	118.3	6.58	386	0.48	14.89	3.72
63530	A11	A11-12	09/25/06	142.1	6.28	344	0.43	14.53	3.71
63410	A3	A3-Ambient	09/18/06	-72	7.56	445	0.00	17.41	3.61
63411	A3	A3-Ambient	09/19/06	-48	7.58	431	0.00	17.65	3.54
63412	A3	A3-Ambient	09/20/06	-24	6.99	404	0.11	17.54	3.54

UNH #	Well	Sample Name	Date	Time (hr)	pH	EC ( $\mu\text{S cm}^{-1}$ )	Br <sup>-</sup> (mg L <sup>-1</sup> )	Na <sup>+</sup> (mg L <sup>-1</sup> )	SO <sub>4</sub> <sup>2-</sup> (mg L <sup>-1</sup> )
63344	A3	A3-Ambient	09/21/06	-1.5	7.22	434	0.06	17.76	3.79
63345	A3	A3-GW Soln	09/21/06	.	7.95	447	6.53	22.36	3.82
63346	A3	A3-Start	09/21/06	0	7.96	436	6.53	22.34	3.84
63347	A3	A3-Leftover	09/21/06	0.1	.	.	5.66	19.62	3.33
63348	A3	A3-1	09/21/06	0.5	7.9	437	5.53	21.38	3.79
63349	A3	A3-2	09/21/06	1	7.8	436	4.35	21.58	3.74
63350	A3	A3-3	09/21/06	1.5	7.83	439	2.96	19.69	3.78
63351	A3	A3-4	09/21/06	2	7.88	438	2.14	18.81	3.74
63352	A3	A3-5	09/21/06	3	7.43	440	1.22	18.44	3.66
63353	A3	A3-6	09/21/06	5.7	7.4	439	0.57	18.03	3.59
63354	A3	A3-7	09/22/06	21.5	7.53	436	0.11	17.67	3.84
63355	A3	A3-8	09/23/06	45.5	6.93	427	0.07	17.80	3.81
63356	A3	A3-9	09/24/06	69.6	7.14	426	0.08	17.63	3.67
63357	A3	A3-10	09/25/06	93.3	7.02	435	0.08	17.40	3.76
63358	A3	A3-11	09/26/06	117.4	7.01	417	0.06	17.52	3.78
63526	A3	A3-12	09/27/06	141.5	7.01	433	0.00	17.69	3.95
63413	A12	A12-Ambient	09/21/06	-72	6.58	380	0.07	17.66	3.55
63414	A12	A12-Ambient	09/20/06	-48	6.75	393	0.11	17.56	3.39
63415	A12	A12-Ambient	09/21/06	-24	6.71	389	0.00	17.63	3.40
63359	A12	A12-Ambient	09/22/06	-1.5	7.15	401	0.06	17.51	3.83
63360	A12	A12-GW Soln	09/22/06	.	7.46	421	6.66	21.78	3.59
63361	A12	A12-Start	09/22/06	0	6.97	413	6.72	22.04	3.65
63362	A12	A12-Leftover	09/22/06	0.1	.	.	6.73	21.89	3.66
63363	A12	A12-1	09/22/06	0.5	7.17	412	6.28	21.62	3.65
63364	A12	A12-2	09/22/06	1	7.2	410	5.81	21.31	3.64
63365	A12	A12-3	09/22/06	1.5	7.22	412	5.11	20.92	3.62
63366	A12	A12-4	09/22/06	2	7.24	414	4.33	20.34	3.61
63367	A12	A12-5	09/22/06	3	7.04	416	3.70	19.92	3.59
63368	A12	A12-6	09/22/06	5.6	6.93	410	3.25	19.85	3.59

UNH #	Well	Sample Name	Date	Time (hr)	pH	EC ( $\mu\text{S cm}^{-1}$ )	Br <sup>-</sup> (mg L <sup>-1</sup> )	Na <sup>+</sup> (mg L <sup>-1</sup> )	SO <sub>4</sub> <sup>2-</sup> (mg L <sup>-1</sup> )
63369	A12	A12-7	09/23/06	21.8	6.12	391	1.27	18.72	3.55
63370	A12	A12-8	09/23/06	29.6	6.73	388	0.94	18.50	3.56
63371	A12	A12-9	09/24/06	45.9	6.44	383	0.42	17.95	3.52
63372	A12	A12-10	09/25/06	69.6	6.56	389	0.20	17.79	3.49
63373	A12	A12-11	09/26/06	93.7	6.79	389	0.15	17.50	3.54
63527	A12	A12-12	09/27/06	117.8	6.8	388	0.14	17.62	3.53
63416	A1	A1-Ambient	09/20/06	-72	6.85	408	0.00	17.69	3.60
63417	A1	A1-Ambient	09/21/06	-48	6.91	412	0.00	18.14	3.59
63418	A1	A1-Ambient	09/22/06	-24	6.79	401	0.12	18.10	3.65
63374	A1	A1-Ambient	09/23/06	-1.5	6.67	376	0.05	17.11	3.21
63375	A1	A1-GW Soln	09/23/06	.	7.28	408	6.74	21.29	3.58
63376	A1	A1-Start	09/23/06	0	6.76	368	6.08	21.70	3.61
63377	A1	A1-Leftover	09/23/06	0	.	.	5.38	17.78	3.01
63378	A1	A1-1	09/23/06	0.3	6.71	373	5.08	20.92	3.60
63379	A1	A1-2	09/23/06	0.5	6.74	374	3.77	19.71	3.56
63380	A1	A1-3	09/23/06	0.8	6.75	374	3.04	19.03	3.62
63381	A1	A1-4	09/23/06	1	6.77	375	2.51	19.22	3.54
63382	A1	A1-5	09/23/06	1.5	6.79	376	1.72	18.56	3.60
63383	A1	A1-6	09/23/06	2	6.8	378	1.33	18.56	3.62
63384	A1	A1-7	09/23/06	3	6.9	385	1.06	17.81	3.59
63385	A1	A1-8	09/23/06	5.6	6.91	393	0.15	18.22	3.71
63386	A1	A1-9	09/24/06	22	6.48	394	0.14	18.13	3.82
63387	A1	A1-10	09/24/06	29.7	7	400	0.70	18.11	3.65
63388	A1	A1-11	09/25/06	45.6	6.7	404	0.14	17.98	3.75
63389	A1	A1-12	09/26/06	69.8	6.94	402	0.13	17.51	3.76
63390	A1	A1-13	09/27/06	93.9	6.71	373	0.13	17.80	3.78
63528	A1	A1-14	09/28/06	118.1	6.55	417	0.13	17.91	3.80

# APPENDIX E

## 2<sup>nd</sup> glucose addition dissolved oxygen (DO), nitrate (NO<sub>3</sub><sup>-</sup>), ammonium (NH<sub>4</sub><sup>+</sup>), total dissolved nitrogen (TDN), and dissolved organic carbon (DOC) concentrations

UNH #	Well	Sample Name	Date	Time (hr)	DO (mg L <sup>-1</sup> )	NO <sub>3</sub> <sup>-</sup> (mg N L <sup>-1</sup> )	NH <sub>4</sub> <sup>+</sup> (µg N L <sup>-1</sup> )	TDN (mg N L <sup>-1</sup> )	DOC (mg C L <sup>-1</sup> )
63958	A11	A11-Ambient	10/22/06	-72	5.01	0.37	36	0.69	6.56
63959	A11	A11-Ambient	10/23/06	-48	5.53	0.23	23	0.53	9.19
63960	A11	A11-Ambient	10/24/06	-24	5.16	0.39		0.61	5.48
63942	A11	A11-Ambient	10/25/06	-1.5	5.51	0.40	18	1.28	5.71
63943	A11	A11-GW Soln	10/25/06	.	5.10	6.02	22	8.46	106.85
63944	A11	A11-Start	10/25/06	0	4.47	5.49	19	8.46	106.85
63945	A11	A11-Leftover	10/25/06	0	3.90	5.52	17	8.60	112.88
63946	A11	A11-1	10/25/06	0.5	4.97	5.44	22	8.40	111.57
63947	A11	A11-2	10/25/06	1	4.76	5.01	24	7.58	96.01
63948	A11	A11-3	10/25/06	1.5	4.27	4.52	32	6.63	77.00
63949	A11	A11-4	10/25/06	2	4.55	4.16	39	5.95	69.37
63950	A11	A11-5	10/25/06	3	4.36	3.34	25	4.25	47.56
63951	A11	A11-6	10/25/06	6.1	3.69	2.92	29	4.13	44.47
63952	A11	A11-7	10/26/06	28.7	3.07	2.25	28	2.55	26.93
63953	A11	A11-8	10/27/06	52.4	3.86	1.68	28	2.18	19.15
63954	A11	A11-9	10/28/06	76.4	3.65	0.98	23	1.10	9.42
63955	A11	A11-10	10/29/06	100.4	4.95	0.07	25	0.39	7.83
63956	A11	A11-11	10/30/06	124.5	5.00	0.10	37	0.44	6.89
63957	A11	A11-12	10/31/06	148.5	4.38	0.20	48	0.48	5.21
64072	A3	A3-Ambient	10/30/06	-72	5.34	1.57	47	1.60	0.27

UNH #	Well	Sample Name	Date	Time (hr)	DO (mg L <sup>-1</sup> )	NO <sub>3</sub> <sup>-</sup> (mg N L <sup>-1</sup> )	NH <sub>4</sub> <sup>+</sup> (µg N L <sup>-1</sup> )	TDN (mg N L <sup>-1</sup> )	DOC (mg C L <sup>-1</sup> )
64073	A3	A3-Ambient	10/31/06	-48	5.32	1.57	28	1.64	0.25
64074	A3	A3-Ambient	11/01/06	-24	5.66	1.60	20	1.71	0.42
64075	A3	A3-Ambient	11/02/06	-1.5	6.78	1.59	17	1.62	0.31
64076	A3	A3-GW Soln	11/02/06	.	6.55	6.09	31	5.71	69.14
64077	A3	A3-Leftover	11/02/06	0	7.50	5.90	20	6.11	68.93
64078	A3	A3-Start	11/02/06	0	8.04	5.63	18	5.70	66.57
64079	A3	A3-1	11/02/06	0.5	7.13	5.07	11	5.18	53.87
64080	A3	A3-2	11/02/06	1	6.85	3.31	17	3.48	28.76
64081	A3	A3-3	11/02/06	1.5	6.80	2.53	23	2.67	13.12
64082	A3	A3-4	11/02/06	2	6.52	2.28	18	2.39	11.29
64083	A3	A3-5	11/02/06	3	6.07	2.10	15	2.31	8.03
64084	A3	A3-6	11/02/06	5.8	5.98	1.72	22	1.95	2.73
64085	A3	A3-7	11/03/06	22.5	6.13	1.54	33	1.68	0.18
64086	A3	A3-8	11/04/06	46.2	6.03	1.59	27	1.77	0.12
64087	A3	A3-9	11/05/06	70.2	6.08	1.57	17	1.75	0.36
64088	A3	A3-10	11/06/06	94.5	5.28	1.58	21	1.70	0.12
64089	A3	A3-11	11/07/06	118.1	4.08	1.54	20	1.65	0.33
64090	A3	A3-12	11/08/06	142	4.36	1.63	15	1.73	0.29
64091	A12	A12-Ambient	11/01/06	-72	6.27	2.01	35	2.21	0.71
64092	A12	A12-Ambient	11/02/06	-48	7.78	2.10	18	2.20	0.33
64093	A12	A12-Ambient	11/03/06	-24	7.74	2.12	40	2.17	0.51
64094	A12	A12-Ambient	11/04/06	-1.5	8.67	2.07	6	2.17	0.47
64095	A12	A12-GW Soln	11/04/06	.	8.43	5.98	24	5.74	62.84
64096	A12	A12-Leftover	11/04/06	0	8.16	4.66	26	5.91	56.70
64097	A12	A12-Start	11/04/06	0	7.98	6.04	11	6.11	63.06
64098	A12	A12-1	11/04/06	0.5	7.74	5.16	22	5.25	51.40
64099	A12	A12-2	11/04/06	1	7.47	3.85	21	4.31	36.44
64100	A12	A12-3	11/04/06	1.5	7.49	4.11	13	3.90	32.33
64101	A12	A12-4	11/04/06	2	7.96	3.71	9	3.60	25.99



UNH #	Well	Sample Name	Date	Time (hr)	DO (mg L <sup>-1</sup> )	NO <sub>3</sub> <sup>-</sup> (mg N L <sup>-1</sup> )	NH <sub>4</sub> <sup>+</sup> (μg N L <sup>-1</sup> )	TDN (mg N L <sup>-1</sup> )	DOC (mg C L <sup>-1</sup> )
64102	A12	A12-5	11/04/06	3	7.34	3.22	9	3.50	17.85
64103	A12	A12-6	11/04/06	5.9	6.96	2.92	15	3.00	17.07
64104	A12	A12-7	11/05/06	22.5	6.88	2.19	0	2.37	2.78
64105	A12	A12-8	11/06/06	46.7	5.93	2.04	0	2.18	0.52
64106	A12	A12-9	11/07/06	70.4	4.47	2.05	9	2.12	0.48
64107	A12	A12-10	11/08/06	94.3	4.44	2.10	0	2.28	0.50
64108	A12	A12-11	11/09/06	118.7	5.18	2.16	17	2.16	0.40
64109	A12	A12-12	11/10/06	142.7	5.14	2.12	20	2.13	0.64
64110	A1	A1-Ambient	11/02/06	-72	6.15	1.99	15	1.98	0.74
64111	A1	A1-Ambient	11/03/06	-48	6.94	2.08	13	2.08	0.60
64112	A1	A1-Ambient	11/04/06	-24	5.76	1.73	58	1.81	0.76
64113	A1	A1-Ambient	11/05/06	-1.5	6.82	1.86	23	1.71	0.70
64114	A1	A1-GW Soln	11/05/06	.	6.63	6.27	27	6.56	74.13
64115	A1	A1-Leftover	11/05/06	0	7.30	6.06	17	5.82	67.15
64116	A1	A1-Start	11/05/06	0	7.25	6.10	18	5.88	66.50
64117	A1	A1-1	11/05/06	0.3	6.88	4.93	23	5.10	46.81
64118	A1	A1-2	11/05/06	0.5	7.15	4.40	19	4.04	36.10
64119	A1	A1-3	11/05/06	0.8	7.32	3.91	37	3.96	32.35
64120	A1	A1-4	11/05/06	1	7.40	3.35	18	3.37	24.54
64121	A1	A1-5	11/05/06	1.5	7.29	3.12	18	3.21	20.79
64122	A1	A1-6	11/05/06	2	7.04	3.01	22	3.18	17.74
64123	A1	A1-7	11/05/06	3	7.05	2.70	26	2.80	12.23
64124	A1	A1-8	11/05/06	6	6.49	2.33	16	2.48	5.26
64125	A1	A1-9	11/06/06	22.9	5.34	2.12	7	2.19	0.55
64126	A1	A1-10	11/07/06	46.6	4.34	1.93	9	2.06	0.50
64127	A1	A1-11	11/08/06	70.5	4.40	1.93	10	2.02	0.52
64128	A1	A1-12	11/09/06	94.9	4.59	2.02	10	2.02	0.51
64129	A1	A1-13	11/10/06	118.9	4.28	1.88	14	1.93	0.69

## APPENDIX F

**2<sup>nd</sup> glucose addition pH, specific conductivity (EC), bromide (Br<sup>-</sup>), sodium (Na<sup>+</sup>), and sulfate (SO<sub>4</sub><sup>2-</sup>) concentrations**

UNH #	Well	Sample Name	Date	Time (hr)	pH	EC ( $\mu\text{s cm}^{-1}$ )	Br <sup>-</sup> (mg L <sup>-1</sup> )	Na <sup>+</sup> (mg L <sup>-1</sup> )	SO <sub>4</sub> <sup>2-</sup> (mg L <sup>-1</sup> )
63958	A11	A11-Ambient	10/22/06	-72	6.59	313	0.31	12.88	2.82
63959	A11	A11-Ambient	10/23/06	-48	6.36	288	0.17	11.93	2.58
63960	A11	A11-Ambient	10/24/06	-24	6.53	335	0.14	13.02	2.64
63942	A11	A11-Ambient	10/25/06	-1.5	7.05	353	0.18	14.40	3.06
63943	A11	A11-GW Soln	10/25/06	.	7.65	461	21.01	28.27	3.41
63944	A11	A11-Start	10/25/06	0	7.71	457	19.88	28.48	3.48
63945	A11	A11-Leftover	10/25/06	0	7.6	.	20.06	28.46	3.51
63946	A11	A11-1	10/25/06	0.5	7.64	433	19.78	28.15	3.49
63947	A11	A11-2	10/25/06	1	7.6	441	17.89	25.49	3.39
63948	A11	A11-3	10/25/06	1.5	7.5	431	16.17	24.28	3.30
63949	A11	A11-4	10/25/06	2	7.43	414	14.91	23.25	3.31
63950	A11	A11-5	10/25/06	3	7.15	408	11.76	20.90	3.17
63951	A11	A11-6	10/25/06	6.1	7	376	9.95	19.92	3.15
63952	A11	A11-7	10/26/06	28.7	6.87	381	7.35	18.01	3.21
63953	A11	A11-8	10/27/06	52.4	6.93	382	5.37	17.02	3.31
63954	A11	A11-9	10/28/06	76.4	6.63	372	3.31	15.46	3.17
63955	A11	A11-10	10/29/06	100.4	6.14	216	0.13	8.55	1.66
63956	A11	A11-11	10/30/06	124.5	6.54	249	0.26	9.59	1.91
63957	A11	A11-12	10/31/06	148.5	6.48	266	0.44	11.18	2.17
64072	A3	A3-Ambient	10/30/06	-72	7.23	445	0.12	17.87	3.59
64073	A3	A3-Ambient	10/31/06	-48	7.52	421	0.00	17.92	3.59
64074	A3	A3-Ambient	11/01/06	-24	7.24	406	0.00	17.80	3.52

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UNH #	Well	Sample Name	Date	Time (hr)	pH	EC ( $\mu\text{S cm}^{-1}$ )	Br <sup>-</sup> (mg L <sup>-1</sup> )	Na <sup>+</sup> (mg L <sup>-1</sup> )	SO <sub>4</sub> <sup>2-</sup> (mg L <sup>-1</sup> )
64075	A3	A3-Ambient	11/02/06	-1.5	6.62	442	0.00	17.49	3.65
64076	A3	A3-GW Soln	11/02/06	.	6.93	502	20.27	29.98	3.83
64077	A3	A3-Leftover	11/02/06	0	7.15	504	19.55	30.07	3.78
64078	A3	A3-Start	11/02/06	0	7.03	446	18.21	28.76	3.73
64079	A3	A3-1	11/02/06	0.5	7.04	449	15.81	26.60	3.69
64080	A3	A3-2	11/02/06	1	6.97	454	8.02	22.26	3.73
64081	A3	A3-3	11/02/06	1.5	7.06	452	4.39	20.10	3.88
64082	A3	A3-4	11/02/06	2	7.08	453	3.34	19.41	3.87
64083	A3	A3-5	11/02/06	3	7.09	452	2.34	18.74	3.91
64084	A3	A3-6	11/02/06	5.8	7.11	447	0.93	17.98	3.91
64085	A3	A3-7	11/03/06	22.5	7.1	448	0.05	17.44	3.90
64086	A3	A3-8	11/04/06	46.2	7.06	448	0.07	18.22	4.01
64087	A3	A3-9	11/05/06	70.2	6.98	447	0.08	17.35	3.99
64088	A3	A3-10	11/06/06	94.5	7.54	414	0.10	17.32	3.93
64089	A3	A3-11	11/07/06	118.1	7.18	415	0.09	17.26	4.05
64090	A3	A3-12	11/08/06	142	7.16	420	0.06	17.40	3.94
64091	A12	A12-Ambient	11/01/06	-72	6.82	377	0.00	17.14	3.18
64092	A12	A12-Ambient	11/02/06	-48	6.53	394	0.00	16.88	3.03
64093	A12	A12-Ambient	11/03/06	-24	6.86	391	0.00	16.96	2.98
64094	A12	A12-Ambient	11/04/06	-1.5	6.87	395	0.00	16.88	3.16
64095	A12	A12-GW Soln	11/04/06	.	6.91	449	18.69	27.50	3.36
64096	A12	A12-Leftover	11/04/06	0	6.99	449	14.63	22.10	2.73
64097	A12	A12-Start	11/04/06	0	6.85	399	18.73	27.68	3.41
64098	A12	A12-1	11/04/06	0.5	6.8	402	14.68	25.41	3.36
64099	A12	A12-2	11/04/06	1	6.83	418	9.84	20.35	2.96
64100	A12	A12-3	11/04/06	1.5	6.85	412	9.75	22.48	3.46
64101	A12	A12-4	11/04/06	2	6.84	410	7.86	21.09	3.40
64102	A12	A12-5	11/04/06	3	6.83	410	5.55	20.04	3.38
64103	A12	A12-6	11/04/06	5.9	6.81	403	3.94	19.55	3.35

UNH #	Well	Sample Name	Date	Time (hr)	pH	EC ( $\mu\text{s cm}^{-1}$ )	Br <sup>-</sup> (mg L <sup>-1</sup> )	Na <sup>+</sup> (mg L <sup>-1</sup> )	SO <sub>4</sub> <sup>2-</sup> (mg L <sup>-1</sup> )
64104	A12	A12-7	11/05/06	22.5	6.68	382	0.76	17.31	3.42
64105	A12	A12-8	11/06/06	46.7	7.01	360	0.13	16.76	3.42
64106	A12	A12-9	11/07/06	70.4	6.79	360	0.07	16.73	3.40
64107	A12	A12-10	11/08/06	94.3	6.85	365	0.08	16.93	3.20
64108	A12	A12-11	11/09/06	118.7	6.58	354	0.11	17.14	3.15
64109	A12	A12-12	11/10/06	142.7	6.72	365	0.03	17.11	3.30
64110	A1	A1-Ambient	11/02/06	-72	6.41	397	0.00	16.53	3.33
64111	A1	A1-Ambient	11/03/06	-48	6.86	399	0.00	16.75	3.31
64112	A1	A1-Ambient	11/04/06	-24	6.81	385	0.07	15.64	3.13
64113	A1	A1-Ambient	11/05/06	-1.5	6.67	371	0.03	16.28	3.06
64114	A1	A1-GW Soln	11/05/06	.	6.97	453	19.96	28.77	3.44
64115	A1	A1-Leftover	11/05/06	0	7	453	19.24	27.90	3.34
64116	A1	A1-Start	11/05/06	0	6.73	390	19.35	28.48	3.44
64117	A1	A1-1	11/05/06	0.3	6.67	393	14.20	24.95	3.39
64118	A1	A1-2	11/05/06	0.5	6.8	397	11.41	23.48	3.44
64119	A1	A1-3	11/05/06	0.8	6.67	396	9.27	22.14	3.56
64120	A1	A1-4	11/05/06	1	6.7	399	6.98	20.65	3.55
64121	A1	A1-5	11/05/06	1.5	6.66	403	5.94	20.06	3.47
64122	A1	A1-6	11/05/06	2	6.69	402	5.01	19.49	3.50
64123	A1	A1-7	11/05/06	3	6.77	401	3.44	18.64	3.58
64124	A1	A1-8	11/05/06	6	6.75	401	1.46	17.65	3.63
64125	A1	A1-9	11/06/06	22.9	7.12	374	0.09	16.57	3.21
64126	A1	A1-10	11/07/06	46.6	6.98	367	0.07	16.28	3.22
64127	A1	A1-11	11/08/06	70.5	6.96	363	0.07	16.14	3.22
64128	A1	A1-12	11/09/06	94.9	6.79	369	0.09	16.37	3.32
64129	A1	A1-13	11/10/06	118.9	6.79	345	0.05	16.25	3.18